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Polysulfonylamines. CX.† Hydroxylammonium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1) and 2-aminopyridinium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1)

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Abstract

In the formula unit of hydroxylammonium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1), H₃NOH⁺·C₂H₆NO₄S₂⁻·C₁₂H₂₄O₆, the 1,4,7,10,13,16-hexaoxacyclooctadecane ring adopts a pseudo-*D*_{3d} conformation. The hydroxylammonium cation forms an O—H···N⁻ hydrogen bond to the anion [O···N 2.677 (2) Å and O—H···N 171 (3)°] and three well defined N⁺—H···O bonds to alternate polyether O atoms. The ammonium N atom is displaced by 0.981 (2) Å from the best O₆ plane of the crown, in contrast to the analogous perchlorate hemihydrate [Trueblood, Knobler, Lawrence & Stevens (1982). *J. Am. Chem. Soc.* **104**, 1355–1362], where the corresponding distance is only 0.68 Å and the H atoms of the NH₃⁺ group were found to be disordered (at 115 K). In the formula unit of 2-aminopyridinium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1), C₅H₇N₂⁺·C₂H₆NO₄S₂⁻·C₁₂H₂₄O₆, the 18-crown-6 ring also adopts a pseudo-*D*_{3d} conformation. The pyridinium donor of the cation forms a markedly bent N—H···O hydrogen bond to the anion [N···O 2.868 (2) Å and N—H···O 150 (2)°], whereas the exocyclic NH₂ group is connected to opposite pairs of crown O atoms *via* two three-centre N—H(···O)₂ interactions. The amino N atom is displaced by 1.531 (2) Å from the best O₆ plane of the crown.

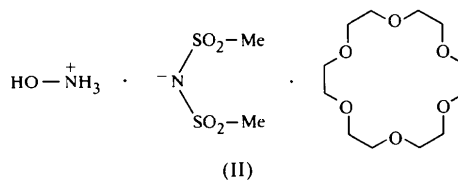
Comment

We are currently engaged in a systematic study of hydrogen-bond patterns in crystalline onium di(methanesulfonyl)amidates. The anion common to these

compounds, (MeSO₂)₂N⁻, is derived from a strong N—H acid (p*K*_a = 0.9, relative to water; Ali *et al.*, 1980) and adopts a fairly rigid solid-state conformation of pseudo- or (more rarely) crystallographic C₂ symmetry, exhibiting two stereochemically different pairs of O atoms characterized by *trans*- and *gauche*-O—S—N—S torsion angles, respectively (Henschel, Moers *et al.*, 1997). Thus, three of its five potential hydrogen-bond acceptors are included in a nearly planar O—S—N—S—O sequence, which, when combined with complementary cationic donor species, provides a robust supramolecular synthon (Desiraju, 1995) for constructing hydrogen-bonding patterns of tunable complexity (Henschel, 1996; Wijaya, 1999).

In contrast to the unique structure of 1-aza-4-azoniabicyclo[2.2.2]octane di(methanesulfonyl)amidate, (I), where no traditional hydrogen bonding is observed between the cation and the anion (Henschel, Moers *et al.*, 1997), the complex hydroxylammonium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1), (II), exemplifies the prototypical case of a single O—H···N⁻ bond accepted by the anion in question. Furthermore, comparison of (II) with the known structure of the analogous perchlorate hemihydrate [(III); Trueblood *et al.*, 1982] offers the possibility of examining perturbations of the cation–crown geometry when the anion is varied.

In the formula unit of (II) (Fig. 1), the hydroxylammonium entity adopts a conformation nearer to eclipsed than staggered [N2—O5 1.410 (2) Å, H01—O5—N2 104 (2)° and H01—O5—N2—H03 16 (3)°]. It forms a relatively short and linear O—H···N⁻ bond to the anion and is linked by three less pronounced N⁺—H···O interactions to the 18-crown-6 macrocycle (hydrogen-bonding geometry in Table 1). It is noteworthy that reference compound (III), where the OH group is connected to the lattice water [H···OW 1.88 (3), O···OW 2.744 (2) Å and O—H···OW 167 (2)°], displays a hydroxylammonium–crown connectivity highly dissimilar from that observed in the present case (see below).



The geometric parameters of the anion, including torsion angles, are similar to those found for (I) and are therefore not given explicitly here. The S1—N1—S2 angle at the hydrogen-bond acceptor N atom [120.87 (11)°] is slightly but significantly larger than in (I) [118.87 (13)°]; as found for two polymorphs of (MeSO₂)₂NH (Blaschette *et al.*, 1994), protonation of

† Part CIX: Moers *et al.* (1999).

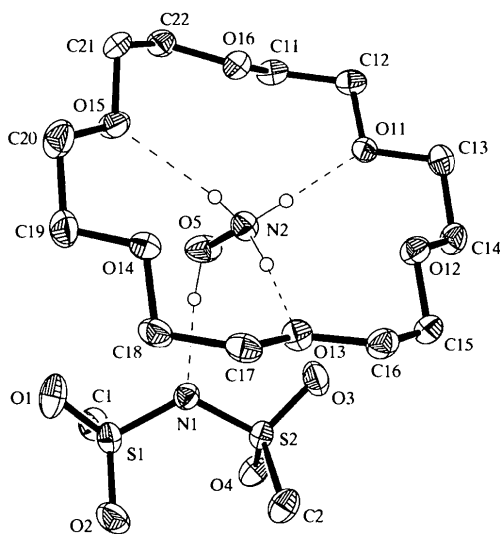


Fig. 1. The structure of compound (II) in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary and dashed lines indicate hydrogen-bonding interactions.

the anion increases the same angle to 125.44(10) or 126.38(8)°. Concomitantly, the π order of the S—N bonds decreases [mean S—N bond lengths: 1.597(2) in (I), 1.6072(18) in (II), and 1.651(2) and 1.6493(14) Å in (MeSO₂)₂NH]. For (II), the H01···N1—S1 and H01···N1—S2 angles are 122(1) and 113(1)°, respectively, conferring upon the N atom an approximately trigonal-planar environment.

As in (III), the symmetry of the macrocycle approximates to D_{3d} , with all C—C torsion angles *gauche* and alternating in sign, and all C—O and O—C torsion angles *trans*. The observed bond lengths (average C—O 1.424 Å and C—C 1.495 Å), bond angles (average C—O—C 112.0° and C—C—O 108.9°) and torsion angles (average absolute values C—O—C—C 175.1° and O—C—C—O 65.0°) lie in the commonly found ranges (Goldberg, 1989a). The distances of the ether O atoms from their best plane are as follows (all $\sigma = 0.0010$ Å): O11 0.2983, O13 0.2147, O15 0.0982, O12 -0.3130, O14 -0.1093 and O16 -0.1889 Å.

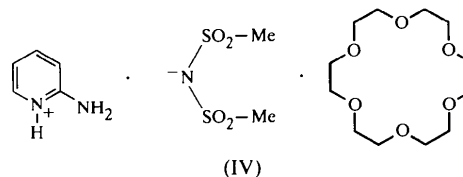
The structural features of the hydroxylammonium-crown complex are essentially similar to those observed for a series of 1:1 complexes between 18-crown-6 and primary alkylammonium salts (Henschel, Blaschette & Jones, 1997, and references therein). The triangle of alternating crown O atoms lying nearer to the NH₃⁺ group forms N⁺—H···O hydrogen bonds with angles of 171(3), 160(3) and 144(3)° (Table 1). The N⁺···O distances to the other three O atoms are also short and indicative of strong dipolar attractions [3.076(2), 2.978(2) and 2.988(2) Å from N2 to O12, O14 and O16, respectively]. The N atom is displaced by 0.778(2) Å from the former O₃ plane, 1.183(2) Å from the latter and 0.981(2) Å from the best plane of

all six crown O atoms. The angle between O5—N2 and the normal to the latter plane is 22.6°.

In contrast to these findings, the ammonium N atom in (III) lies only 0.68 Å from the best O₆ plane of the crown ring. The H atoms of the NH₃⁺ group are disordered over two sets of positions, and the set of H atoms that could be definitely located is involved in three-centre interactions, each H atom binding to two adjacent O atoms [all N···O ≤ 2.918(3) Å, all N—H···O ≤ 147(3)°; data recorded at 115 K]. Moreover, the tilt angle of the O—N bond relative to the O₆ plane is remarkably small (5.6°). Thus, depending on the specific interactions with the counter-ion assemblage (X⁻), the NH₃⁺ group is displaced from a clearly 'perching' position for X⁻ = (MeSO₂)₂N⁻ to a position intermediate between 'perching' and 'nesting' for X⁻ = $\frac{1}{2}$ H₂O·ClO₄⁻ (for definitions see Cram & Trueblood, 1981).

The structure of (II) was routinely checked for C—H···O hydrogen bonds; the shortest contacts (H···O ≤ 2.60 Å) are included in Table 1.

As a sequel to the structure of (II), where the NH₃⁺ donor group is complexed and shielded by the coronand and the OH group forms a single O—H···N⁻ bond to the anion, we also present here the structure of the complex 2-aminopyridinium di(methanesulfonyl)amidate 1,4,7,10,13,16-hexaoxacyclooctadecane (1/1/1), (IV), which involves a single N—H···O cation-to-anion connectivity.



In the formula unit of (IV) (Fig. 2), the exocyclic amino group is attached *via* two three-centre N—H(···O)₂ interactions to opposite pairs of crown O atoms, whereas the pyridinium donor forms a markedly bent hydrogen bond to a sulfonyl O atom of the anion (hydrogen-bonding geometries in Table 2).

The bond lengths, angles and torsion angles of the anion again do not deviate appreciably from normal values (see above). In the present case, the hydrogen-bond-acceptor atom O1 is of the *trans* type [O1—S1—N1—S2 -169.60(11)°, H01···O1—S1 124(1)° and O1—S1 1.4580(15) Å, compared with 1.440–1.441 Å for the other O—S bonds].

The geometric features of the heterocyclic cation are very similar to those found for the cations in the structures of 2-aminopyridinium salicylate (Gellert & Hsu, 1988) and propynoate (Wheeler & Foxman, 1994). In particular, the C—N bond length from the amino nitrogen to the ring [N3—C3 1.323(3) Å] is

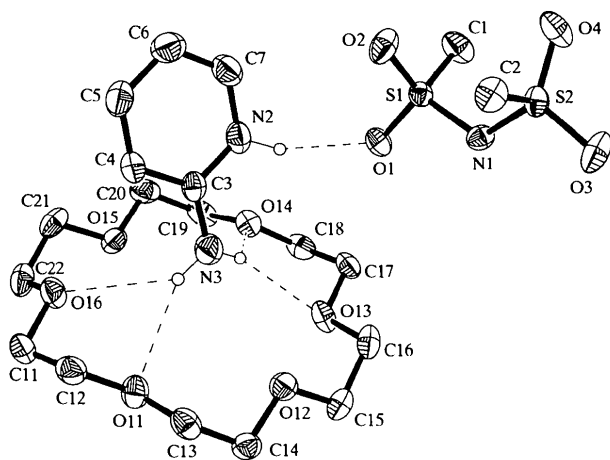


Fig. 2. The structure of compound (IV) in the crystal. Ellipsoids represent 50% probability levels. Only selected H atoms are shown (see text). H-atom radii are arbitrary and dashed lines indicate hydrogen-bonding interactions.

significantly shorter than the N—C distances within the ring [N2—C3 1.358 (3) and N2—C7 1.362 (3) Å]. The sum of the angles around N3 [357 (2)°] establishes the predominantly sp^2 character of that atom. According to this evidence, the cation appears to be in the iminium resonance form, binding with the NH_2^+ group to the crown ether.

The symmetry of the macrocycle again approximates to D_{3d} (see above), with normal observed bond lengths (average C—O 1.421 Å and C—C 1.494 Å), angles (average C—O—C 112.5° and C—C—O 108.7°) and torsion angles (average absolute values C—O—C—C 175.1° and O—C—C—O 69.6°). The distances of the ether O atoms from their best plane are as follows: O12 0.1338 (10), O14 0.2825 (10), O16 0.2443 (10), O11 -0.1577 (11), O13 -0.1967 (11) and O15 -0.3061 (11) Å.

The angle between C3—N3 and the normal to the best O_6 plane of the macrocycle is 31.4°; the N3 atom is displaced by 1.531 (2) Å from this plane. To identify the three-centre hydrogen bonds (Table 2), a default cutoff of 2.60 Å for the $\text{H} \cdots \text{O}$ distance was used. The $\text{N3} \cdots \text{O}(\text{crown})$ distances associated with these interactions lie in the range 3.14–3.31 Å, but the distances of N3 to the other two crown O atoms are of similar magnitude [$\text{N3} \cdots \text{O12}$ 3.080 (3) Å and $\text{N3} \cdots \text{O15}$ 3.325 (3) Å]. Solid-state structures of related complexes between 18-crown-6 and neutral or positively charged NH_2 donor species have been reviewed (Goldberg, 1989b).

The crystal structure of (IV) comprises a number of C—H \cdots O contacts that could be classified as hydrogen bonds; only the most prominent ($\text{H} \cdots \text{O} \leq 2.60$ Å) are included in Table 2. The shortest occurs within the asymmetric unit and links a crown CH_2 group to the

same atom (O1) that accepts the traditional hydrogen bond.

Experimental

For the preparation of (II), hydroxylammonium di(methanesulfonyl)amidate, (V), hitherto unreported, was prepared by refluxing a suspension of $[\text{NH}_3\text{OH}]\text{Cl}$ (0.248 g, 3.57 mmol) and $\text{Ag}[\text{N}(\text{SO}_2\text{Me})_2]$ (1.00 g, 3.57 mmol) in anhydrous ethanol (20 ml) for 3 h. After removing AgCl by filtration, the filtrate was evaporated under reduced pressure at room temperature. The colourless solid residue was recrystallized from a minimum amount of hot MeCN. Crystalline (V) separated in a yield of 95% (0.70 g; m.p. 359–366 K). Complex (II) formed as a colourless flaky solid on adding diethyl ether to a solution of (V) (0.300 g, 1.45 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (0.383 g, 1.45 mmol) in anhydrous MeCN (20 ml). The crude product was isolated and redissolved in a minimum amount of hot acetonitrile/diethyl ether (1/1) and the solution cooled very slowly to room temperature. The crystals, obtained in 70% yield (0.48 g), were suitable for X-ray analysis; melting interval 415–435 K. ^1H NMR (CD_3CN , 200 MHz) for (II): δ 2.84 (s, 6H, CH_3), 3.65 (s, 24H, CH_2), 8.74 (sbr, 4H, $\text{NH} + \text{OH}$); for (V): δ 2.85 (s, 6H, CH_3), 7.57 (sbr, 4H, $\text{NH} + \text{OH}$). Satisfactory elemental analyses were obtained for (II) and (V). For the preparation of (IV), 2-aminopyridinium di(methanesulfonyl)amidate was prepared from equimolar amounts of 2-aminopyridine and $(\text{MeSO}_2)_2\text{NH}$ according to a known procedure (Lange, 1994). A solution of this compound (2.67 g, 10.0 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (2.64 g, 10.0 mmol) in anhydrous methanol (15 ml) was cooled to 275 K for several days. The crystals which separated in a yield of 77% (4.1 g) were suitable for X-ray analysis (m.p. 358–363 K). ^1H NMR (CD_3CN , 200 MHz): δ 2.96 (s, 6H, CH_3), 3.50 (s, 24H, CH_2), 6.78–6.96 and 7.79–7.95 (2H and 2H, aromatic H), $\delta(\text{NH})$ not detected. A satisfactory elemental analysis was obtained.

Compound (II)

Crystal data

$\text{H}_4\text{NO}^+ \cdot \text{C}_2\text{H}_6\text{NO}_4\text{S}_2^- \cdot$
 $\text{C}_{12}\text{H}_{24}\text{O}_6$
 $M_r = 470.55$
 Orthorhombic
Pbca
 $a = 18.5888$ (12) Å
 $b = 8.1378$ (10) Å
 $c = 28.964$ (2) Å
 $V = 4381.4$ (7) Å³
 $Z = 8$
 $D_x = 1.427$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 64 reflections
 $\theta = 3.0$ – 12.5°
 $\mu = 0.300$ mm⁻¹
 $T = 173$ (2) K
 Tablet
 $0.5 \times 0.5 \times 0.2$ mm
 Colourless

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: none
 3848 measured reflections
 3848 independent reflections
 2631 reflections with
 $I > 2\sigma(I)$

$\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 22$
 $k = -9 \rightarrow 1$
 $l = -34 \rightarrow 0$
 3 standard reflections
 every 247 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.074$
 $S = 0.883$
 3848 reflections
 281 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0382P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. *Hydrogen-bonding geometry* (\AA , $^\circ$) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H01...N1	0.93 (3)	1.76 (3)	2.677 (2)	171 (3)
N2—H02...O11	0.912 (18)	1.972 (19)	2.876 (2)	171 (3)
N2—H03...O13	0.919 (18)	2.05 (2)	2.930 (2)	160 (3)
N2—H04...O15	0.924 (19)	2.11 (2)	2.911 (2)	144 (3)
C22—H22B...O16'	0.99	2.52	3.282 (3)	134.0
C15—H15B...O3	0.99	2.56	3.395 (3)	142.2

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$.**Compound (IV)***Crystal data*

$C_5H_7N_2 \cdot C_2H_6NO_4S_2^- \cdot$
 $C_{12}H_{24}O_6$
 $M_r = 531.64$
 Monoclinic
 $P2_1/n$
 $a = 11.670$ (3) \AA
 $b = 15.623$ (5) \AA
 $c = 14.528$ (4) \AA
 $\beta = 108.74$ (3) $^\circ$
 $V = 2508.2$ (12) \AA^3
 $Z = 4$
 $D_x = 1.408$ Mg m $^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ \AA
 Cell parameters from 50
 reflections
 $\theta = 10.0$ – 11.5°
 $\mu = 0.269$ mm $^{-1}$
 $T = 143$ (2) K
 Tablet
 $0.6 \times 0.5 \times 0.3$ mm
 Colourless

Data collection

Stoe Stadi-4 diffractometer
 ω/θ scans
 Absorption correction: none
 4790 measured reflections
 4431 independent reflections
 3668 reflections with
 $I > 2\sigma(I)$
 $R_{int} = 0.022$

$\theta_{max} = 25.02^\circ$
 $h = -13 \rightarrow 13$
 $k = -18 \rightarrow 1$
 $l = 0 \rightarrow 17$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.094$
 $S = 1.061$
 4431 reflections
 322 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2$
 $+ 1.2421P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.33$ e \AA^{-3}
 $\Delta\rho_{min} = -0.40$ e \AA^{-3}
 Extinction correction:
SHELXL97
 Extinction coefficient:
 0.0115 (6)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 2. *Hydrogen-bonding geometry* (\AA , $^\circ$) for (IV)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H01...O1	0.94 (3)	2.01 (3)	2.868 (2)	150 (2)
N3—H02...O11	0.854 (19)	2.44 (2)	3.222 (3)	152 (2)
N3—H02...O16	0.854 (19)	2.51 (2)	3.217 (3)	140 (2)
N3—H03...O13	0.85 (2)	2.48 (2)	3.301 (3)	162 (2)
N3—H03...O14	0.85 (2)	2.55 (2)	3.144 (3)	128 (2)
C17—H17B...O1	0.99	2.45	3.428 (3)	171.7
C2—H2C...O1'	0.98	2.59	3.508 (3)	155.1
C13—H13B...O12 ⁱⁱ	0.99	2.60	3.585 (3)	176.8
C19—H19B...O2 ⁱⁱⁱ	0.99	2.59	3.552 (3)	165.5

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

For compound (II), H atoms of NH and OH groups were refined freely (but with N—H bond lengths restrained to be equal), methyl H atoms were identified from difference Fourier syntheses and were refined as part of rigid groups allowed to rotate but not tip, and the remaining H atoms were refined as riding. Although the freely refined H atoms have slightly large U values (0.072–0.099 \AA^2), they were clearly identified from difference syntheses (peaks of 0.43–0.51 e \AA^{-3}). There were no final residual peaks greater than 0.13 e \AA^{-3} near N2. For (IV), H(N) atoms were refined freely but with N—H bond lengths restrained to be equal. Other H atoms were refined as for compound (II).

Data collection: XSCANS (Fait, 1991) for (II); DIF4 (Stoe & Cie, 1992a) for (IV). Cell refinement: XSCANS for (II); DIF4 for (IV). Data reduction: XSCANS for (II); REDU4 (Stoe & Cie, 1992b) for (IV). For both compounds, program(s) used to solve structures: SHELXS97 (Sheldrick, 1990); program(s) used to refine structures: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1316). Services for accessing these data are described at the back of the journal.

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2-(2,3-Diphenylpiperazin-1-yl)ethylammonium chloride

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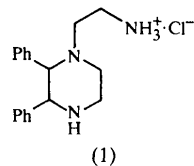
Abstract

In the title compound ($\text{C}_{18}\text{H}_{24}\text{N}_3^+\text{Cl}^-$), the hydrochloride of a substituted piperazine, the amino-N atom is protonated. The conformation at the ethyl-C atoms is *gauche*, with the two phenyl groups approximately orthogonal to the piperazine ring. The crystal structure is stabilized by hydrogen bonds involving the chloride ion and the protonated N atom.

Comment

Piperazine and its derivatives form an important class of organic compounds with versatile chelating ability (Marzotto *et al.*, 1998) and pharmacological applications (Liu *et al.*, 1998). Some metal complexes of piperazine are also known for their antitumoural activity (Ciccarese

et al., 1998). During our ongoing programme of the synthesis and reactivity of imidazo[1,2-*a*]pyrazines, the title compound, (1), a hydrochloric acid salt of a diphenylpiperazine derivative, was obtained. The crystal structure determination of (1) was undertaken to elucidate the molecular conformation.



The bond lengths and angles in (1) are comparable to those observed in related piperazine derivatives (Parihar *et al.*, 1995; Thirumurugan *et al.*, 1998; Tyrseleva *et al.*, 1995; Okamoto *et al.*, 1992). The torsion angle C1—C7—C12—C13 is 58.6(3)°, corresponding to a *gauche* conformation at C7—C12. The piperazine ring adopts a chair conformation with the N1 and N2 atoms deviating by 0.743(3) and 0.585(3) Å, respectively, on opposite sides of the least-squares plane through C7, C8, C9 and C12 [maximum deviation of an in-plane atom 0.016(4) Å]. The two phenyl rings (C1—C6 and C13—C18) are inclined at 37.8(1)° to each other and at angles of 97.8(2) and 95.3(2)° to the piperazine ring. The amino-N atom (N3) is protonated. The crystal packing is stabilized by a network of hydrogen bonds (Table 2) involving the chloride ion and the protonated N (N3) atom.

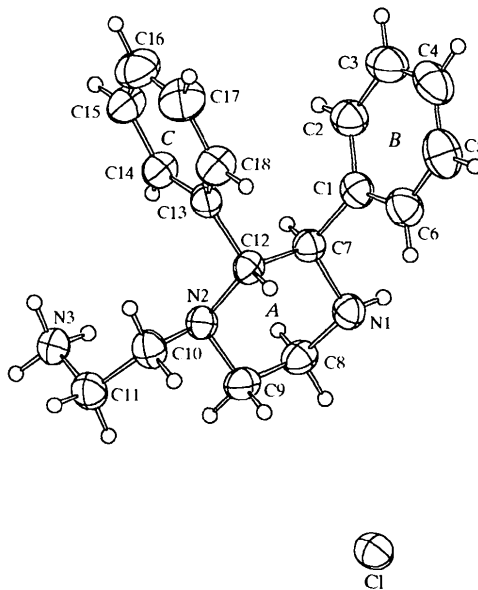


Fig. 1. A ZORTEP (Zsolnai, 1995) view of (1) showing 50% probability displacement ellipsoids for the non-H atoms. H atoms are shown as circles of an arbitrary radius.