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Piperazin-1-ium 4-aminobenzoate monohydrate

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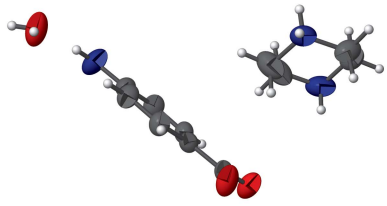
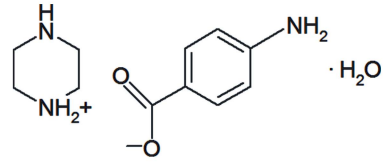
The asymmetric unit of the title hydrated salt, $C_4H_{11}N_2^+\cdot C_7H_6NO_2^-\cdot H_2O$, contains a piperazin-1-ium cation, a 4-aminobenzoate anion and a water molecule. One NH group of the piperazine ring is protonated and this ring adopts a chair conformation. The anion of this salt is generated by deprotonation of the OH group of the carboxylic acid substituent of 4-aminobenzoic acid. The benzene ring makes a dihedral angle of 2.6 (2)° with the carboxylate substituent. The anion and the solvent water molecule are linked by an N—H···O hydrogen bond. Additional N—H···O and O—H···O hydrogen bonds connect adjacent anions through the water molecules, generating a two-dimensional network parallel to (100), forming $R_3^3(12)$ ring motifs. Adjacent cations are linked by N—H···N hydrogen bonds into infinite chains along (001). These chains are linked to the two-dimensional network of anions and water molecules by another N—H···O hydrogen bond, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

In a continuation of our studies of piperazine derivatives, which are known to exhibit anti-bacterial, antimalarial (Chaudhary *et al.*, 2006) and antimicrobial (Kharb *et al.*, 2012) activity, we report herein the synthesis and crystal structure of the title compound, Fig. 1.

The asymmetric unit contains a piperazin-1-ium cation, a 4-amino benzoate anion and a water molecule. In this organic salt, one NH group of the piperazine ring is protonated while the OH group of the carboxylic acid substituent of 4-amino benzoic acid is deprotonated. The bond lengths are in normal ranges and comparable to those found in a related structure (Wei, 2011). The piperazinium ring adopts a chair conformation, with puckering parameters $Q = 0.547$ (3) Å, $\theta = 180.0$ (3), $\psi = 23$ (3)°. The C1–C6 benzene ring

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O3	0.86	2.19	3.027 (3)	165
N1—H1A···O2^{i}	0.86	2.12	2.962 (2)	168
N2—H2A···N1^{ii}	0.88 (1)	2.57 (2)	3.335 (3)	147 (2)
N3—H3A···N2^{iii}	0.90	1.92	2.793 (2)	165
N3—H3B···O1^{iv}	0.90	1.84	2.726 (2)	166
O3—H3C···O2^{v}	0.83 (1)	1.91 (1)	2.737 (2)	176 (4)
O3—H3D···O1^{vi}	0.83 (1)	1.95 (1)	2.776 (2)	177 (3)

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

in the anion subtends a dihedral angle of 2.6 (2)° to the carboxylate (O1/C7/O2) substituent.

In the asymmetric unit, the anion and water molecule are linked *via* an intermolecular N1—H1B···O3 hydrogen bond. Additional N—H···O and O—H···O hydrogen bonds, Table 1, connect the anions through water molecules into a two-dimensional network parallel to (100) and generates an $R_3^3(12)$ ring motif, Fig. 2. The cations are linked by an N—

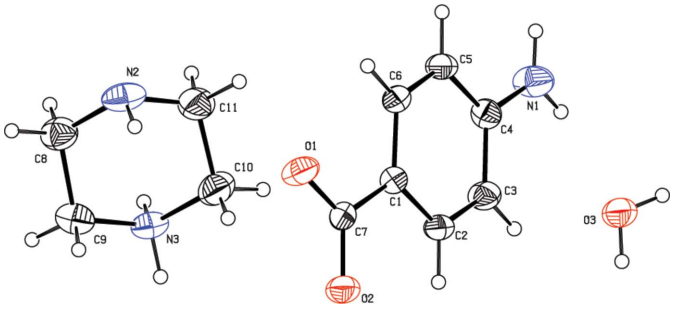


Figure 1
The asymmetric unit of the title molecular salt, showing the atom labelling and 30% probability displacement ellipsoids.

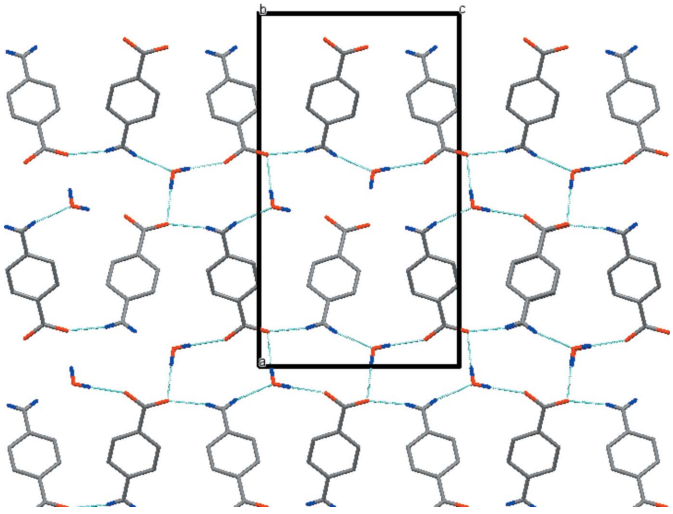


Figure 2
A partial view of the crystal packing, showing the $R_3^3(12)$ ring motif. The hydrogen bonds are shown as dashed lines (see Table 1) and C-bound H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_{11}N_2^+·C_7H_6NO_2^-·H_2O$
M_r	241.29
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	295
a, b, c (Å)	18.2964 (14), 7.1388 (6), 10.3574 (6)
V (Å^3)	1352.83 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.28 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.976, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15633, 2648, 1981
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.091, 1.06
No. of reflections	2648
No. of parameters	167
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, −0.12

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

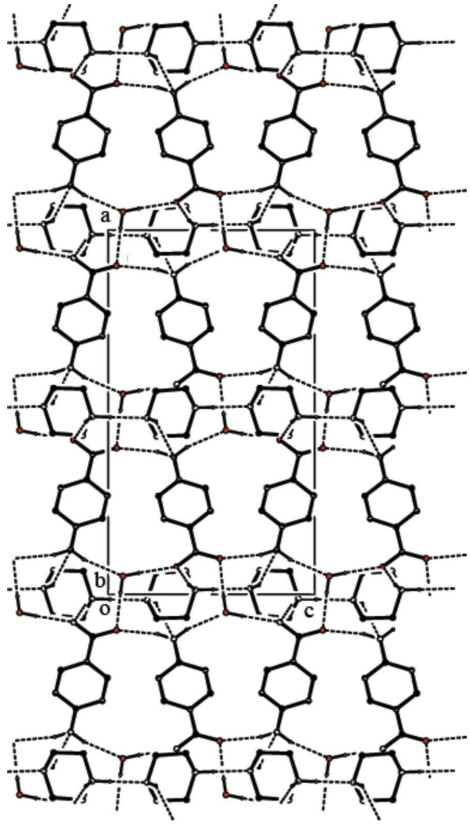


Figure 3
The crystal packing of the title compound, viewed along the b axis.

H···N hydrogen bond into infinite chains along (001). These cation chains are also linked to the two-dimensional network of anions and water molecules by an N3—H3*B*···O1 hydrogen bond, forming a three-dimensional network, Fig. 3.

Synthesis and crystallization

The title compound was synthesized from 4-amino-benzoic acid (1.828 g) and piperazine (1.148 g) in an equimolar ratio. The reactants were dissolved in 10 ml of acetone and the solvent was allowed to slowly evaporate at room temperature. After one week, crystals suitable for X-ray diffraction were obtained.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_4H_{11}N_2^+·C_7H_6NO_2^-·H_2O$
M_r = 241.29
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 18.2964 (14) Å
b = 7.1388 (6) Å
c = 10.3574 (6) Å
V = 1352.83 (17) Å^3
Z = 4
$F(000)$ = 520
D_x = 1.185 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5261 reflections
θ = 2.2–25.9°
μ = 0.09 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.976, T_{max} = 0.983
15633 measured reflections
2648 independent reflections
1981 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 26.0°, θ_{min} = 2.2°
h = −22→22
k = −8→8
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.091
S = 1.06
2648 reflections
167 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.1919P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0150 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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_{iso}*/U_{eq}
C1	0.68490 (11)	0.8943 (3)	0.39677 (18)	0.0397 (5)
C2	0.72877 (11)	0.8264 (3)	0.49587 (19)	0.0456 (5)
H2	0.7151	0.8482	0.5811	0.055*
C3	0.79165 (12)	0.7279 (3)	0.4713 (2)	0.0498 (6)
H3	0.8200	0.6843	0.5395	0.060*
C4	0.81335 (11)	0.6927 (3)	0.34408 (19)	0.0443 (5)
C5	0.77022 (11)	0.7605 (3)	0.24516 (19)	0.0468 (5)
H5	0.7837	0.7387	0.1599	0.056*
C6	0.70757 (11)	0.8600 (3)	0.27110 (19)	0.0431 (5)
H6	0.6797	0.9053	0.2028	0.052*
C7	0.61580 (11)	0.9950 (3)	0.4256 (2)	0.0421 (5)
C8	0.43405 (14)	0.4288 (4)	0.2356 (2)	0.0613 (7)
H8A	0.4465	0.3101	0.1958	0.074*
H8B	0.3846	0.4606	0.2097	0.074*
C9	0.43638 (14)	0.4070 (4)	0.3798 (2)	0.0588 (7)
H9A	0.4188	0.5208	0.4206	0.071*
H9B	0.4047	0.3048	0.4058	0.071*
C10	0.56413 (18)	0.5115 (4)	0.3763 (2)	0.0717 (8)
H10A	0.6136	0.4750	0.3989	0.086*
H10B	0.5537	0.6305	0.4175	0.086*
C11	0.55779 (16)	0.5321 (4)	0.2312 (3)	0.0713 (8)
H11A	0.5898	0.6323	0.2029	0.086*
H11B	0.5742	0.4172	0.1904	0.086*
N1	0.87752 (10)	0.5984 (3)	0.31881 (19)	0.0653 (6)
H1A	0.8913	0.5809	0.2404	0.078*
H1B	0.9038	0.5570	0.3815	0.078*
N2	0.48383 (14)	0.5724 (3)	0.18885 (18)	0.0634 (6)
N3	0.51219 (11)	0.3684 (3)	0.42236 (16)	0.0506 (5)
H3A	0.5135	0.3644	0.5092	0.061*
H3B	0.5260	0.2554	0.3925	0.061*
O1	0.57619 (8)	1.0491 (2)	0.33263 (13)	0.0584 (4)
O2	0.59834 (8)	1.0228 (3)	0.54085 (13)	0.0615 (5)
O3	0.94991 (10)	0.4935 (3)	0.57142 (17)	0.0714 (5)
H2A	0.4749 (15)	0.677 (2)	0.231 (2)	0.083 (10)*
H3C	0.9945 (6)	0.492 (5)	0.560 (4)	0.109 (12)*
H3D	0.9410 (16)	0.508 (4)	0.6489 (12)	0.084 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0390 (11)	0.0435 (12)	0.0365 (11)	−0.0028 (10)	0.0000 (9)	−0.0025 (9)
C2	0.0447 (12)	0.0605 (14)	0.0315 (11)	0.0010 (11)	0.0013 (9)	−0.0008 (10)
C3	0.0497 (13)	0.0617 (16)	0.0380 (11)	0.0075 (12)	−0.0032 (10)	0.0070 (10)
C4	0.0435 (12)	0.0434 (13)	0.0459 (12)	0.0040 (10)	0.0021 (10)	0.0007 (10)
C5	0.0494 (12)	0.0581 (15)	0.0329 (10)	0.0028 (12)	0.0040 (9)	−0.0011 (10)
C6	0.0413 (11)	0.0540 (15)	0.0341 (11)	−0.0007 (11)	−0.0039 (9)	0.0019 (9)
C7	0.0370 (12)	0.0505 (13)	0.0387 (11)	−0.0024 (10)	−0.0021 (9)	−0.0057 (10)
C8	0.0640 (15)	0.0687 (18)	0.0510 (14)	0.0107 (13)	−0.0036 (12)	0.0046 (12)
C9	0.0678 (16)	0.0578 (16)	0.0509 (13)	0.0121 (13)	0.0104 (11)	0.0066 (12)
C10	0.093 (2)	0.0741 (19)	0.0479 (14)	−0.0296 (16)	−0.0116 (13)	0.0068 (13)
C11	0.088 (2)	0.076 (2)	0.0495 (15)	−0.0304 (16)	0.0042 (14)	0.0085 (13)
N1	0.0639 (13)	0.0832 (15)	0.0486 (11)	0.0303 (12)	0.0019 (10)	0.0007 (11)
N2	0.1045 (18)	0.0488 (13)	0.0371 (10)	0.0057 (13)	0.0009 (11)	0.0033 (10)
N3	0.0736 (13)	0.0448 (10)	0.0335 (9)	0.0042 (10)	−0.0001 (9)	0.0006 (8)
O1	0.0590 (9)	0.0783 (12)	0.0379 (8)	0.0226 (8)	−0.0080 (8)	−0.0100 (8)
O2	0.0460 (8)	0.1006 (13)	0.0378 (9)	0.0128 (9)	0.0010 (7)	−0.0088 (8)
O3	0.0476 (11)	0.1231 (16)	0.0434 (10)	0.0115 (11)	−0.0006 (8)	−0.0115 (10)

Geometric parameters (Å, º)

C1—C6	1.388 (3)	C9—N3	1.481 (3)
C1—C2	1.390 (3)	C9—H9A	0.9700
C1—C7	1.485 (3)	C9—H9B	0.9700
C2—C3	1.372 (3)	C10—N3	1.475 (3)
C2—H2	0.9300	C10—C11	1.514 (3)
C3—C4	1.399 (3)	C10—H10A	0.9700
C3—H3	0.9300	C10—H10B	0.9700
C4—N1	1.379 (3)	C11—N2	1.451 (4)
C4—C5	1.381 (3)	C11—H11A	0.9700
C5—C6	1.375 (3)	C11—H11B	0.9700
C5—H5	0.9300	N1—H1A	0.8600
C6—H6	0.9300	N1—H1B	0.8600
C7—O2	1.252 (2)	N2—H2A	0.878 (10)
C7—O1	1.265 (2)	N3—H3A	0.9000
C8—N2	1.454 (3)	N3—H3B	0.9000
C8—C9	1.502 (3)	O3—H3C	0.825 (10)
C8—H8A	0.9700	O3—H3D	0.825 (10)
C8—H8B	0.9700		
C6—C1—C2	117.26 (18)	C8—C9—H9A	109.7
C6—C1—C7	121.92 (17)	N3—C9—H9B	109.7
C2—C1—C7	120.80 (17)	C8—C9—H9B	109.7
C3—C2—C1	121.72 (18)	H9A—C9—H9B	108.2
C3—C2—H2	119.1	N3—C10—C11	109.8 (2)
C1—C2—H2	119.1	N3—C10—H10A	109.7

C2—C3—C4	120.33 (19)	C11—C10—H10A	109.7
C2—C3—H3	119.8	N3—C10—H10B	109.7
C4—C3—H3	119.8	C11—C10—H10B	109.7
N1—C4—C5	121.14 (18)	H10A—C10—H10B	108.2
N1—C4—C3	120.55 (19)	N2—C11—C10	113.0 (2)
C5—C4—C3	118.28 (18)	N2—C11—H11A	109.0
C6—C5—C4	120.83 (17)	C10—C11—H11A	109.0
C6—C5—H5	119.6	N2—C11—H11B	109.0
C4—C5—H5	119.6	C10—C11—H11B	109.0
C5—C6—C1	121.59 (18)	H11A—C11—H11B	107.8
C5—C6—H6	119.2	C4—N1—H1A	120.0
C1—C6—H6	119.2	C4—N1—H1B	120.0
O2—C7—O1	122.08 (19)	H1A—N1—H1B	120.0
O2—C7—C1	119.08 (18)	C11—N2—C8	110.1 (2)
O1—C7—C1	118.84 (18)	C11—N2—H2A	101.1 (19)
N2—C8—C9	112.7 (2)	C8—N2—H2A	108.4 (19)
N2—C8—H8A	109.0	C10—N3—C9	112.22 (19)
C9—C8—H8A	109.0	C10—N3—H3A	109.2
N2—C8—H8B	109.0	C9—N3—H3A	109.2
C9—C8—H8B	109.0	C10—N3—H3B	109.2
H8A—C8—H8B	107.8	C9—N3—H3B	109.2
N3—C9—C8	109.97 (19)	H3A—N3—H3B	107.9
N3—C9—H9A	109.7	H3C—O3—H3D	110 (3)

C6—C1—C2—C3	−0.5 (3)	C6—C1—C7—O2	−179.6 (2)
C7—C1—C2—C3	177.9 (2)	C2—C1—C7—O2	2.0 (3)
C1—C2—C3—C4	−0.1 (3)	C6—C1—C7—O1	0.8 (3)
C2—C3—C4—N1	178.2 (2)	C2—C1—C7—O1	−177.6 (2)
C2—C3—C4—C5	0.4 (3)	N2—C8—C9—N3	−55.7 (3)
N1—C4—C5—C6	−177.8 (2)	N3—C10—C11—N2	54.9 (3)
C3—C4—C5—C6	0.0 (3)	C10—C11—N2—C8	−55.8 (3)
C4—C5—C6—C1	−0.7 (3)	C9—C8—N2—C11	56.3 (3)
C2—C1—C6—C5	0.9 (3)	C11—C10—N3—C9	−53.9 (3)
C7—C1—C6—C5	−177.5 (2)	C8—C9—N3—C10	54.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O3	0.86	2.19	3.027 (3)	165
N1—H1*A*···O2^{i}	0.86	2.12	2.962 (2)	168
N2—H2*A*···N1^{ii}	0.88 (1)	2.57 (2)	3.335 (3)	147 (2)
N3—H3*A*···N2^{iii}	0.90	1.92	2.793 (2)	165
N3—H3*B*···O1^{iv}	0.90	1.84	2.726 (2)	166
O3—H3*C*···O2^{v}	0.83 (1)	1.91 (1)	2.737 (2)	176 (4)
O3—H3*D*···O1^{vi}	0.83 (1)	1.95 (1)	2.776 (2)	177 (3)

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