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Piperazine-1,4-diium bis(4-nitrobenzoate) dihydrate

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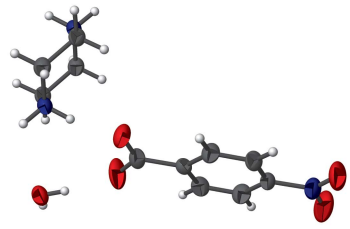
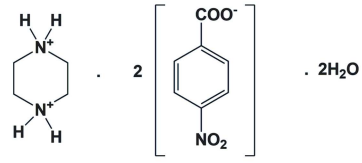
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title molecular salt, $C_4H_{12}N_2^{2+}\cdot 2C_7H_4NO_4^{-}\cdot 2H_2O$, is composed of half a protonated piperazine dication, located about an inversion center, a benzoate anion and a water molecule of crystallization. In the crystal, the various units are linked by N—H···O, O—H···O and C—H···O hydrogen bonds, forming a supramolecular three-dimensional framework.

3D view



Chemical scheme



Structure description

Piperazine derivatives are found in a number of biologically active compounds, including several marketed drugs, and the piperazine ring is considered to be a privileged structure in drug discovery (Suzuki *et al.*, 1997). Piperazines are frequently used as building blocks for pharmaceuticals (Kaloustian *et al.*, 1976), and exhibit a substantial degree of selective RNA binding (Dega-Szafran *et al.*, 2002).

The asymmetric unit of the title molecular salt comprises half a protonated piperazine dication, a benzoate anion and a water molecule of crystallization (Fig. 1). The piperazine dication is located about an inversion center and the ring has a chair conformation. The geometric parameters agree well with those reported for a similar compound, piperazine-1,4-diium bis(4-aminobenzenesulfonate) (Kumar *et al.*, 2015).

In the crystal, the various units are linked by N—H···O, O—H···O and C—H···O hydrogen bonds, forming a supramolecular three-dimensional framework (Table 1 and Fig. 2).

Synthesis and crystallization

4.3 g (0.057 mol) of piperazine and 8.4 g (0.029 mol) of 4-nitrobenzoic acid were dissolved in 50 ml of double-distilled water and stirred at room temperature for 5 h to

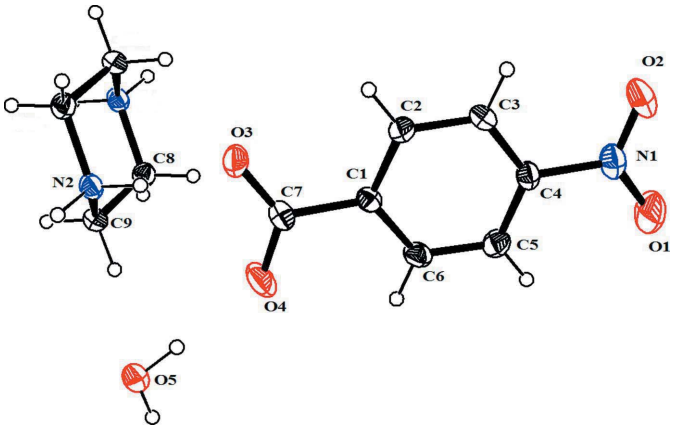


Figure 1
The molecular structure of the title compound, with atom labelling and 30% probability displacement ellipsoids. The unlabelled atoms of the piperazine-1,4-diium dication are related to the labelled atoms by inversion symmetry (symmetry operation: $-x+1, -y+1, -z+2$).

obtain an homogeneous solution. The solution was filtered and allowed to evaporate in a dust-free atmosphere. After a few days, yellow block-like crystals were obtained (yield 94%, m.p. 370 K).

Refinement

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

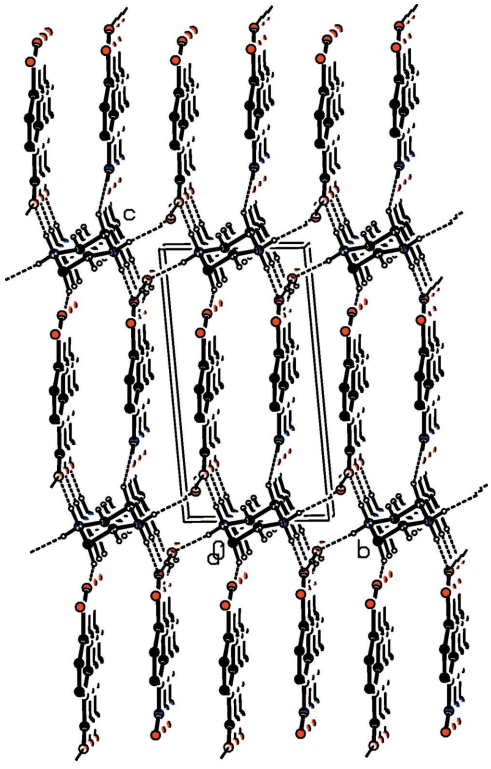


Figure 2
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds (Table 1) are shown as dashed lines, and H atoms not involved in these interactions have been omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3	0.94 (2)	1.82 (2)	2.747 (2)	169 (2)
N2—H2B···O5^{i}	0.92 (2)	1.85 (2)	2.751 (2)	162 (2)
O5—H5A···O4	0.89 (2)	1.85 (2)	2.733 (2)	168 (2)
O5—H5B···O3^{ii}	0.91 (2)	1.88 (2)	2.761 (2)	164 (2)
C8—H8A···O2^{iii}	0.97	2.51	3.326 (3)	141
C9—H9B···O5	0.97	2.52	3.312 (2)	139

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$0.5C_4H_{12}N_2^{2+}\cdot C_7H_4NO_4^-\cdot H_2O$
M_r	228.21
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	6.5793 (5), 6.8094 (5), 12.3767 (9)
α, β, γ (°)	92.085 (4), 99.427 (3), 109.301 (4)
V (Å^3)	513.81 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.20 × 0.20 × 0.15
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.976, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10658, 2019, 1369
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.106, 0.97
No. of reflections	2019
No. of parameters	162
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.17

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171291 [https://doi.org/10.1107/S2414314617012913]

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Crystal data

$0.5C_4H_{12}N_2^{2+}\cdot C_7H_4NO_4^-\cdot H_2O$
M_r = 228.21
Triclinic, $P\overline{1}$
a = 6.5793 (5) Å
b = 6.8094 (5) Å
c = 12.3767 (9) Å
α = 92.085 (4)°
β = 99.427 (3)°
γ = 109.301 (4)°
V = 513.81 (7) Å^3
Z = 2
$F(000)$ = 240
D_x = 1.475 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2927 reflections
θ = 6.2–30.1°
μ = 0.12 mm^{-1}
T = 296 K
Block, yellow
0.20 × 0.20 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.976, T_{max} = 0.982
10658 measured reflections
2019 independent reflections
1369 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 26.0°, θ_{min} = 3.2°
h = −8→8
k = −8→8
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 0.97
2019 reflections
162 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1764P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.069 (7)

Special details

Refinement. The NH_2 and water H atoms were located in difference-Fourier maps and refined with distance restraints: N—H = O—H = 0.90 (2) Å and H···H = 1.48 (2) Å. The C-bound H atoms were fixed geometrically and allowed to ride on their parent atoms: C—H = 0.93 - 0.97 Å with U_{iso}(H) = 1.2U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3881 (3)	0.7745 (2)	0.62147 (14)	0.0307 (4)
C2	0.1832 (3)	0.7949 (3)	0.60281 (15)	0.0380 (5)
H2	0.1225	0.8221	0.6620	0.046*
C3	0.0685 (3)	0.7751 (3)	0.49680 (15)	0.0397 (5)
H3	−0.0688	0.7898	0.4840	0.048*
C4	0.1595 (3)	0.7335 (3)	0.41069 (14)	0.0344 (4)
C5	0.3615 (3)	0.7113 (3)	0.42579 (15)	0.0413 (5)
H5	0.4204	0.6824	0.3663	0.050*
C6	0.4745 (3)	0.7332 (3)	0.53230 (15)	0.0392 (5)
H6	0.6125	0.7199	0.5444	0.047*
C7	0.5200 (3)	0.7940 (3)	0.73631 (15)	0.0380 (5)
C8	0.5409 (3)	0.3454 (3)	0.93267 (14)	0.0353 (4)
H8A	0.4891	0.3739	0.8590	0.042*
H8B	0.5943	0.2294	0.9265	0.042*
C9	0.7243 (3)	0.5354 (3)	0.99088 (15)	0.0354 (4)
H9A	0.7843	0.5032	1.0622	0.042*
H9B	0.8405	0.5752	0.9483	0.042*
N1	0.0338 (3)	0.7086 (3)	0.29788 (13)	0.0487 (5)
N2	0.6427 (2)	0.7116 (2)	1.00540 (12)	0.0334 (4)
O1	0.1169 (3)	0.6756 (3)	0.22173 (13)	0.0826 (6)
O2	−0.1475 (3)	0.7239 (3)	0.28617 (13)	0.0698 (5)
O3	0.4310 (2)	0.8115 (2)	0.81642 (10)	0.0483 (4)
O4	0.7073 (2)	0.7872 (3)	0.74364 (12)	0.0700 (5)
O5	1.0952 (2)	0.9029 (2)	0.88996 (11)	0.0438 (4)
H2A	0.588 (3)	0.752 (3)	0.9379 (12)	0.052 (6)*
H2B	0.753 (3)	0.828 (3)	1.0429 (14)	0.055 (6)*
H5B	1.187 (3)	0.863 (4)	0.8539 (17)	0.071 (8)*
H5A	0.971 (3)	0.884 (4)	0.8424 (17)	0.082 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0281 (9)	0.0282 (9)	0.0337 (10)	0.0086 (7)	0.0028 (7)	0.0026 (7)
C2	0.0356 (10)	0.0517 (12)	0.0316 (10)	0.0195 (9)	0.0099 (8)	0.0041 (8)
C3	0.0273 (10)	0.0534 (12)	0.0394 (11)	0.0165 (9)	0.0026 (8)	0.0067 (9)
C4	0.0359 (10)	0.0337 (10)	0.0284 (10)	0.0080 (8)	−0.0003 (8)	0.0027 (7)
C5	0.0449 (12)	0.0483 (11)	0.0352 (11)	0.0200 (9)	0.0121 (9)	0.0002 (8)
C6	0.0304 (10)	0.0464 (11)	0.0448 (12)	0.0188 (9)	0.0063 (8)	0.0031 (9)
C7	0.0368 (11)	0.0379 (10)	0.0374 (11)	0.0154 (9)	−0.0028 (8)	−0.0002 (8)
C8	0.0370 (10)	0.0389 (10)	0.0308 (10)	0.0148 (8)	0.0053 (8)	−0.0005 (8)

C9	0.0282 (9)	0.0434 (10)	0.0352 (10)	0.0138 (8)	0.0042 (7)	0.0044 (8)
N1	0.0537 (11)	0.0490 (10)	0.0354 (10)	0.0133 (9)	−0.0041 (8)	0.0025 (8)
N2	0.0303 (8)	0.0332 (8)	0.0308 (9)	0.0059 (7)	0.0001 (7)	0.0011 (7)
O1	0.0929 (14)	0.1240 (16)	0.0322 (9)	0.0438 (12)	0.0045 (9)	−0.0088 (9)
O2	0.0550 (10)	0.0952 (13)	0.0524 (10)	0.0289 (9)	−0.0153 (8)	0.0047 (9)
O3	0.0507 (9)	0.0685 (10)	0.0309 (7)	0.0293 (7)	0.0029 (6)	0.0072 (6)
O4	0.0425 (9)	0.1151 (14)	0.0537 (10)	0.0404 (9)	−0.0115 (7)	−0.0104 (9)
O5	0.0361 (8)	0.0481 (8)	0.0389 (8)	0.0074 (7)	0.0006 (6)	−0.0047 (6)

Geometric parameters (Å, º)

C1—C6	1.382 (2)	C8—N2^{i}	1.487 (2)
C1—C2	1.384 (2)	C8—C9	1.505 (3)
C1—C7	1.516 (2)	C8—H8A	0.9700
C2—C3	1.380 (3)	C8—H8B	0.9700
C2—H2	0.9300	C9—N2	1.484 (2)
C3—C4	1.369 (2)	C9—H9A	0.9700
C3—H3	0.9300	C9—H9B	0.9700
C4—C5	1.370 (3)	N1—O1	1.213 (2)
C4—N1	1.474 (2)	N1—O2	1.217 (2)
C5—C6	1.380 (3)	N2—C8^{i}	1.487 (2)
C5—H5	0.9300	N2—H2A	0.940 (14)
C6—H6	0.9300	N2—H2B	0.922 (15)
C7—O4	1.237 (2)	O5—H5B	0.908 (15)
C7—O3	1.252 (2)	O5—H5A	0.892 (16)
C6—C1—C2	118.80 (16)	N2^{i}—C8—H8A	109.6
C6—C1—C7	118.92 (15)	C9—C8—H8A	109.6
C2—C1—C7	122.28 (16)	N2^{i}—C8—H8B	109.6
C3—C2—C1	120.31 (17)	C9—C8—H8B	109.6
C3—C2—H2	119.8	H8A—C8—H8B	108.1
C1—C2—H2	119.8	N2—C9—C8	110.25 (14)
C4—C3—C2	119.09 (17)	N2—C9—H9A	109.6
C4—C3—H3	120.5	C8—C9—H9A	109.6
C2—C3—H3	120.5	N2—C9—H9B	109.6
C3—C4—C5	122.35 (16)	C8—C9—H9B	109.6
C3—C4—N1	118.67 (16)	H9A—C9—H9B	108.1
C5—C4—N1	118.97 (17)	O1—N1—O2	123.50 (18)
C4—C5—C6	117.74 (17)	O1—N1—C4	118.42 (18)
C4—C5—H5	121.1	O2—N1—C4	118.08 (18)
C6—C5—H5	121.1	C9—N2—C8^{i}	111.36 (14)
C5—C6—C1	121.70 (17)	C9—N2—H2A	112.4 (11)
C5—C6—H6	119.1	C8^{i}—N2—H2A	106.2 (12)
C1—C6—H6	119.1	C9—N2—H2B	111.1 (13)
O4—C7—O3	124.85 (17)	C8^{i}—N2—H2B	108.3 (12)
O4—C7—C1	117.09 (17)	H2A—N2—H2B	107.3 (15)
O3—C7—C1	118.05 (16)	H5B—O5—H5A	108.0 (17)
N2^{i}—C8—C9	110.14 (14)		

C6—C1—C2—C3	−0.3 (3)	C6—C1—C7—O4	5.3 (3)
C7—C1—C2—C3	−179.75 (17)	C2—C1—C7—O4	−175.23 (18)
C1—C2—C3—C4	0.5 (3)	C6—C1—C7—O3	−173.33 (17)
C2—C3—C4—C5	−0.2 (3)	C2—C1—C7—O3	6.2 (3)
C2—C3—C4—N1	178.82 (17)	N2^{i}—C8—C9—N2	−56.7 (2)
C3—C4—C5—C6	−0.3 (3)	C3—C4—N1—O1	178.66 (19)
N1—C4—C5—C6	−179.32 (17)	C5—C4—N1—O1	−2.3 (3)
C4—C5—C6—C1	0.5 (3)	C3—C4—N1—O2	−0.8 (3)
C2—C1—C6—C5	−0.3 (3)	C5—C4—N1—O2	178.29 (18)
C7—C1—C6—C5	179.25 (17)	C8—C9—N2—C8^{i}	57.4 (2)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O3	0.94 (2)	1.82 (2)	2.747 (2)	169 (2)
N2—H2*B*···O5^{ii}	0.92 (2)	1.85 (2)	2.751 (2)	162 (2)
O5—H5*A*···O4	0.89 (2)	1.85 (2)	2.733 (2)	168 (2)
O5—H5*B*···O3^{iii}	0.91 (2)	1.88 (2)	2.761 (2)	164 (2)
C8—H8*A*···O2^{iv}	0.97	2.51	3.326 (3)	141
C9—H9*B*···O5	0.97	2.52	3.312 (2)	139

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