organic compounds

Piperazinediium dioxamate

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The title compound, $C_4H_{12}N_2^{2+}\cdot 2C_2H_2NO_3^-$, contains a network of doubly protanated piperazinium cations (lying about centres of inversion) and dioxamate anions. The piperazinium dication adopts a typical chair conformation. The crystal structure is stabilized by cation–to–anion N—H···O and anion–to–anion N—H···O hydrogen bonds.

Related literature

For related structures, see: Büyükgüngör & Odabaşoğlu (2008); Wilkinson & Harrison (2007). For biological applications of piperazines, see: Berkheij *et al.* (2005); Humle & Cherrier (1999). For the synthesis of a ligand with two piperazine arms, see: Bharathi *et al.* (2006). For the use of piperazine derivatives as buffers, see: Good *et al.* (1966). For the piperazine nucleus and its ability to bind to multiple receptors, see: Dinsmore & Beshore (2002).
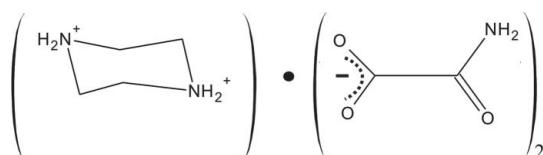
Experimental

Crystal data
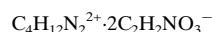
$C_4H_{12}N_2^{2+}\cdot 2C_2H_2NO_3^-$	$V = 564.35$ (6) Å^3
$M_r = 264.25$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.4323$ (4) Å	$\mu = 0.13$ mm^{-1}
$b = 6.7681$ (4) Å	$T = 293$ K
$c = 13.0032$ (7) Å	$0.24 \times 0.22 \times 0.16$ mm
$\beta = 94.488$ (2)°	

Data collection

Bruker APEXII CCD diffractometer	9313 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2606 independent reflections
$T_{min} = 0.969$, $T_{max} = 0.979$	2197 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	3 restraints
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
2606 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}
82 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.86	2.24	3.0232 (9)	152
N1—H1B···O3^{ii}	0.86	2.07	2.8622 (8)	153
N2—H2A···O1^{iii}	0.90	2.37	3.0589 (8)	133
N2—H2A···O2^{iii}	0.90	1.94	2.7475 (9)	149
N2—H2B···O1^{iv}	0.90	1.87	2.7509 (9)	164

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia (1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

References

Berkheij, M., van der Sluis, L., Sewing, C., den Boer, D. J., Terpstra, J. W., Heimstra, H., Bakker, W. I. I., van den Hoogen Band, A. & van Maarseveen, J. H. (2005). *Tetrahedron*, **46**, 2369-2371.
Bharathi, K. S., Rahiman, A. K., Rajesh, K., Sreedaran, S., Aravindan, P. G., Velmurugan, D. & Narayanan, V. (2006). *Polyhedron*, **25**, 2859-2868.
Bruker (2004). *APEX2, SAINT* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, U. S. A.
Büyükgüngör, O. & Odabaşoğlu, M. (2008). *Acta Cryst.* E**64**, o808.
Dinsmore, C. J. & Beshore, D. C. (2002). *Tetrahedron*, **58**, 3297-3312.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Good, N. E., Winget, G. D., Winter, W., Connolly, T. N., Izawa, S. & Singh, R. M. (1966). *Biochemistry*, **5**, 467–477.
Humle, C. & Cherrier, M. P. (1999). *Tetrahedron Lett.* **40**, 5295–5299.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wilkinson, H. S. & Harrison, W. T. A. (2007). *Acta Cryst.* E**63**, m26–m28.
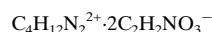
supporting information

Piperazinediium dioxamate

S. Murugavel, R. Selvakumar, S. Govindarajan, P. S. Kannan and A. SubbiahPandi

S1. Comment

Piperazines are among the most important building blocks in today's drug discovery. The piperazine nucleus is capable of binding to multiple receptors with high affinity and therefore piperazine has been classified as a privileged structure (Dinsmore *et al.*, 2002). They are found in biologically active compounds across a number of different therapeutic areas (Berkheij *et al.*, 2005) such as antifungal, antibacterial, antimalarial, antipsychotic, antidepressant and antitumour activity against colon, prostate, breast, lung and leukemia tumors (Humle & Cherrier, 1999). Also Piperazine derivatives are widely used as buffers (Good *et al.*, 1966), and can act as complexing reagents with metal ions (Bharathi *et al.*, 2006). Encouraged by the above information, we report the crystal structure of the title compound, piperazinium bis (dioxamate) (I) (Fig. 1).

In the crystal structure of (I), the piperazinium dication lies on a centre of inversion and adopts a typical chair conformation. The bond lengths in (I) are normal and comparable with the corresponding values observed in the related structure (Wilkinson & Harrison, 2007). The dihedral angle between the piperazinium dication and oxamate anion is 9.54 (3)°. The crystal structure (Fig. 2) is stabilized by cation–to–anion N—H⋯O hydrogen bonds between the N—H atoms of the piperazinium ring and the O atoms of the oxamate (Fig. 2 and Table 1; symmetry code as in Fig. 2). The crystal packing is further stabilized by anion–to–anion N—H⋯O hydrogen bonds between the N—H atoms and the O atoms from the neighbouring oxamate anions (Fig. 2 and Table 1; symmetry code as in Fig. 2). Thus, the symmetry–related molecules are cross linked by these hydrogen bonds to generate a three–dimensional network.

S2. Experimental

Piperazinium bis(dioxamate) was prepared by adding aqueous solution (15ml) of piperazine (0.194g; 0.001mol) to the solution (15ml) of oxamic acid (0.089g; 0.001mol). The resulting clear solution was concentrated over water-bath to half the volume and kept for crystallization at room temperature. The transparent single crystals suitable for x-ray diffraction obtained after two days were filtered off, washed with ethanol and air dried.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with N—H = 0.86–0.90 Å and C—H = 0.97 Å with $U_{iso}(H) = 1.2U_{eq}$.
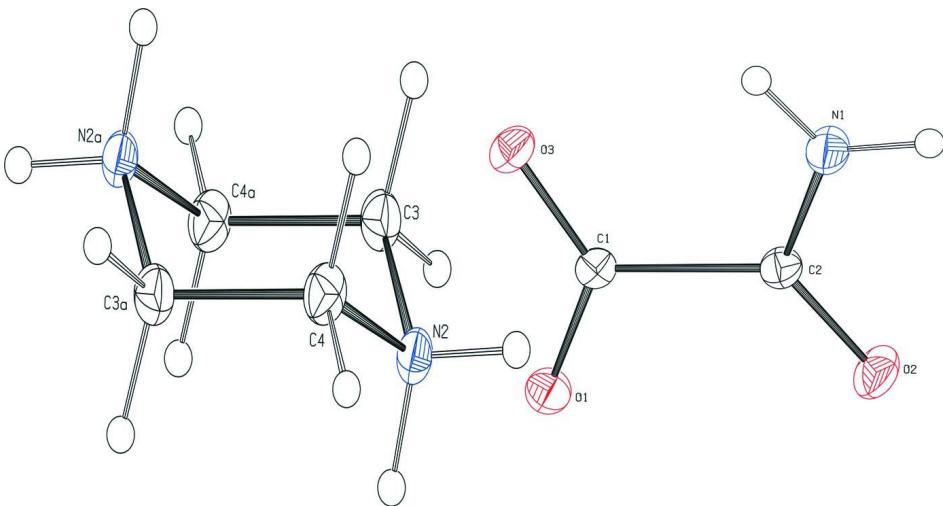
Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small cycles of arbitrary radius.
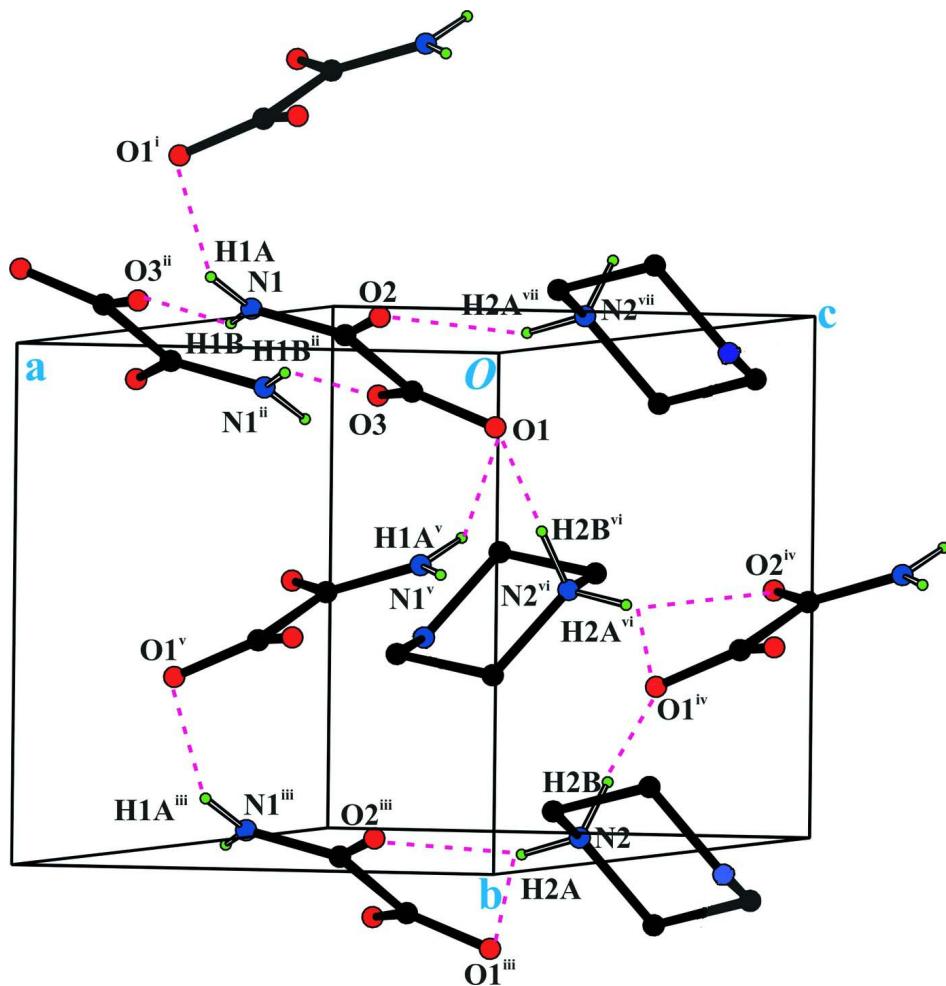
Figure 2

N—H···O hydrogen bonds (dotted lines) in the title compound.[Symmetry code: (i) -x+1, y-1/2, -z+1/2 ; (ii) -x+1, -y, -z; (iii) x, y+1, z; (iv)-x, y+1/2, -z+1/2 (v) -x+1, y+1/2, -z+1/2; (vi) -x, y-1/2, -z+1/2; (vii) x, y-1, z.]

Piperazinediium dioxamate

Crystal data
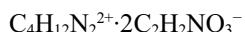
$C_4H_{12}N_2{}^{2+} \cdot 2C_2H_2NO_3{}^-$	$F(000) = 280$
$M_r = 264.25$	$D_x = 1.555$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2743 reflections
$a = 6.4323$ (4) Å	$\theta = 3.1–36.3°$
$b = 6.7681$ (4) Å	$\mu = 0.13$ mm^{-1}
$c = 13.0032$ (7) Å	$T = 293$ K
$\beta = 94.488$ (2)°	Block, colourless
$V = 564.35$ (6) Å^3	$0.24 \times 0.22 \times 0.16$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	9313 measured reflections
Radiation source: fine-focus sealed tube	2606 independent reflections
Graphite monochromator	2197 reflections with $I > 2\sigma(I)$
Detector resolution: 10.0 pixels mm^{-1}	$R_{int} = 0.021$
ω scans	$\theta_{max} = 36.3°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan	$h = -10\rightarrow10$
(*SADABS*; Sheldrick, 1996)	$k = -11\rightarrow10$
$T_{min} = 0.969$, $T_{max} = 0.979$	$l = -20\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.0606P]$
2606 reflections	where $P = (F_o^2 + 2F_c^2)/3$
82 parameters	$(\Delta/\sigma)_{max} < 0.001$
3 restraints	$\Delta\rho_{max} = 0.36$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.34$ e Å^{-3}

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
N2	0.08666 (10)	0.95960 (10)	0.40409 (4)	0.02372 (13)
H2A	0.1752	0.9900	0.3562	0.028*
H2B	0.0161	0.8502	0.3830	0.028*
C3	−0.06294 (12)	1.12524 (12)	0.41301 (5)	0.02590 (15)
H3A	−0.1436	1.1441	0.3475	0.031*
H3B	0.0132	1.2462	0.4297	0.031*
C4	0.20790 (11)	0.91851 (12)	0.50401 (6)	0.02572 (15)
H4A	0.2938	1.0320	0.5240	0.031*
H4B	0.2992	0.8064	0.4962	0.031*
O1	0.13426 (8)	0.15896 (9)	0.19612 (4)	0.02683 (13)
O2	0.44704 (10)	−0.03929 (12)	0.30376 (4)	0.03431 (16)
O3	0.28309 (12)	0.09059 (12)	0.05073 (4)	0.03678 (17)
N1	0.61883 (11)	−0.06196 (13)	0.15969 (5)	0.03142 (17)
H1A	0.7247	−0.1186	0.1917	0.038*
H1B	0.6182	−0.0387	0.0946	0.038*
C1	0.27471 (10)	0.08954 (10)	0.14582 (4)	0.02114 (13)

C2	0.45721 (11)	−0.01070 (11)	0.21043 (5)	0.02200 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0244 (3)	0.0285 (3)	0.0190 (2)	−0.0053 (2)	0.00670 (19)	−0.0034 (2)
C3	0.0285 (3)	0.0280 (3)	0.0214 (3)	−0.0015 (3)	0.0027 (2)	0.0021 (2)
C4	0.0208 (3)	0.0312 (4)	0.0254 (3)	0.0001 (2)	0.0034 (2)	−0.0022 (2)
O1	0.0230 (2)	0.0337 (3)	0.0242 (2)	0.0066 (2)	0.00426 (18)	0.00091 (19)
O2	0.0304 (3)	0.0553 (4)	0.0179 (2)	0.0129 (3)	0.0059 (2)	0.0084 (2)
O3	0.0432 (4)	0.0502 (4)	0.0168 (2)	0.0188 (3)	0.0017 (2)	0.0017 (2)
N1	0.0291 (3)	0.0460 (4)	0.0200 (2)	0.0156 (3)	0.0067 (2)	0.0051 (2)
C1	0.0232 (3)	0.0222 (3)	0.0181 (2)	0.0024 (2)	0.0014 (2)	0.0006 (2)
C2	0.0225 (3)	0.0261 (3)	0.0178 (3)	0.0038 (2)	0.0039 (2)	0.0019 (2)

Geometric parameters (Å, º)

N2—C3	1.4879 (11)	C4—H4B	0.9700
N2—C4	1.4883 (10)	O1—C1	1.2478 (5)
N2—H2A	0.9000	O2—C2	1.2357 (8)
N2—H2B	0.9000	O3—C1	1.2419 (5)
C3—C4ⁱ	1.5095 (10)	N1—C2	1.3205 (9)
C3—H3A	0.9700	N1—H1A	0.8600
C3—H3B	0.9700	N1—H1B	0.8600
C4—C3ⁱ	1.5095 (10)	C1—O3	1.2419 (5)
C4—H4A	0.9700	C1—C2	1.5459 (10)
C3—N2—C4	111.75 (6)	N2—C4—H4B	109.6
C3—N2—H2A	109.3	C3ⁱ—C4—H4B	109.6
C4—N2—H2A	109.3	H4A—C4—H4B	108.1
C3—N2—H2B	109.3	C2—N1—H1A	120.0
C4—N2—H2B	109.3	C2—N1—H1B	120.0
H2A—N2—H2B	107.9	H1A—N1—H1B	120.0
N2—C3—C4ⁱ	110.33 (6)	O3—C1—O1	127.54 (7)
N2—C3—H3A	109.6	O3—C1—O1	127.54 (7)
C4ⁱ—C3—H3A	109.6	O3—C1—C2	116.96 (6)
N2—C3—H3B	109.6	O3—C1—C2	116.96 (6)
C4ⁱ—C3—H3B	109.6	O1—C1—C2	115.50 (5)
H3A—C3—H3B	108.1	O2—C2—N1	123.63 (7)
N2—C4—C3ⁱ	110.48 (6)	O2—C2—C1	120.41 (6)
N2—C4—H4A	109.6	N1—C2—C1	115.96 (5)
C3ⁱ—C4—H4A	109.6		
C4—N2—C3—C4ⁱ	−56.67 (9)	O3—C1—C2—O2	−170.89 (8)
C3—N2—C4—C3ⁱ	56.75 (9)	O1—C1—C2—O2	8.52 (11)
O3—O3—C1—O1	0.00 (4)	O3—C1—C2—N1	8.95 (11)

O3—O3—C1—C2	0.00 (4)	O3—C1—C2—N1	8.95 (11)
O3—C1—C2—O2	−170.89 (8)	O1—C1—C2—N1	−171.64 (7)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1ⁱ	0.86	2.24	3.0232 (9)	152
N1—H1*B*···O3ⁱⁱⁱ	0.86	2.07	2.8622 (8)	153
N2—H2*A*···O1ⁱᵛ	0.90	2.37	3.0589 (8)	133
N2—H2*A*···O2ⁱᵛ	0.90	1.94	2.7475 (9)	149
N2—H2*B*···O1ᵛ	0.90	1.87	2.7509 (9)	164

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