trans-2,5-Dimethylpiperazine-1,4-diium dinitrate

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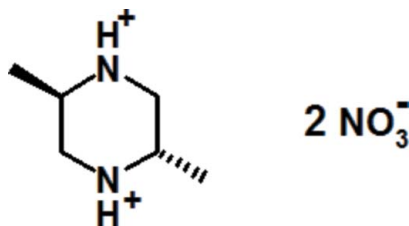Correspondence e-mail: dhaouadihassouna@yahoo.fr

In the structure of the title salt, $C_6H_{16}N_2^{2+}\cdot2NO_3^-$, the cations are connected to the anions through bifurcated N—H$\cdots$(O,O) and weak C—H$\cdots$O hydrogen bonds, generating corrugated layers parallel to the (100) plane. The organic cation is centrosymmetric and the diprotonated piperazine ring adopts a chair conformation, with the methyl groups occupying equatorial positions.

Related literature

For pharmacological properties of piperazine, see: Conrado et al. (2008). For related structures, see: Gatfaoui et al. (2013, 2014a,b); Marouani et al. (2012); Kefi et al. (2013). For a complex of the title cation, see: Rother et al. (1997). For puckering parameters, see: Cremer & Pople (1975).

Experimental

Crystal data

$C_6H_{16}N_2^{2+}\cdot2NO_3^-$	$b = 10.0277$ (10) Å
$M_r = 240.23$	$c = 8.3112$ (8) Å
Monoclinic, $P2_1/c$	$\beta = 116.149$ (8)°
$a = 7.0357$ (8) Å	$V = 526.36$ (9) Å^3

$Z = 2$	$T = 150$ K
Mo $K\alpha$ radiation	$0.58 \times 0.46 \times 0.23$ mm
$\mu = 0.13$ mm^{-1}	

Data collection

Bruker APEXII diffractometer	4126 measured reflections
Absorption correction: multi-scan ($SADABS$; Bruker, 2006) $T_{min} = 0.827$, $T_{max} = 0.970$	1195 independent reflections 1059 reflections with $I > 2\sigma(I)$ $R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	74 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
1195 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O1^i	0.90	1.99	2.8471 (14)	158
N2—H2A$\cdots$O2^{ii}	0.90	2.45	2.9899 (13)	119
N2—H2B$\cdots$O1	0.90	2.07	2.9057 (13)	153
N2—H2B$\cdots$O3	0.90	2.42	3.2172 (14)	149
C1—H1$\cdots$O1^{iii}	0.98	2.50	3.2614 (14)	134

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

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Putz 2005); software used to prepare material for publication: WinGX (Farrugia, 2012) and CRYSCAL (T. Roisnel, local program).

Supporting information for this paper is available from the IUCr electronic archives (Reference: BG2529).

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supporting information

trans-2,5-Dimethylpiperazine-1,4-diium dinitrate

Sofian Gatfaoui, Thierry Roisnel, Hassouna Dhaouadi and Houda Marouani

S1. Comment

Piperazine and its derivatives are widely used due to their interesting biological and pharmacology proprieties (Conrado *et al.*, 2008). In this work, we report the preparation and the structural investigation of a new organic nitrate, $C_6H_{16}N_2 \cdot (NO_3)_2$ (I). The asymmetric unit of (I) is composed of a half *trans*-2,5-dimeyhylpipeazine-1,4-dium cations and one nitrate anion (Figure 1). In the structure, the cations are connected to the anions through bifurcated N—H⋯O(O) and weak C—H⋯O hydrogen bonds, generating a corrugated layers parallel to the (001) plane (Fig. 2).

Interatomic bond lengths and angles of the nitrate anions spread respectively within the ranges [1.2398 (13)–1.2706 (13) Å] and [118.65 (10)–121.73 (10)°]. These geometrical features have also been noticed in other crystal structures (Marouani *et al.*, 2012; Kefi *et al.*, 2013; Gatfaoui *et al.*, 2013, 2014*a*,*b*). It is worth noting that the distance N1—O1 is significantly longer than the N1—O2 and N1—O3 distances because O1 is applied in three hydrogen bonds (table1) while O2 and O3 are applied in only one hydrogen bond. Inside such a structure, the complete organic entity is generated by inversion symmetry located at (0, 0, 0) and (0, 1/2, 1/2). So it is built up by only the half of the cation. Examination of the organic cations shows that the bond distances and angles show no significant difference from those obtained in other complex involving the same organic groups (Rother *et al.*, 1997). The diprotonated piperazine ring adopts a chair conformation, with the methyl groups occupying an equatorial position, with puckering parameters: Q = 0.6083 Å, θ = 90 ° and φ = 166 ° (Cremer & Pople, 1975).

The established H-bonds of types N—H⋯O(O) and C—H⋯O involve oxygen atoms of the nitrate anions as acceptors, and protonated nitrogen atoms and methine groups of the *trans*-2,5-dimethylpiperazine-1,4-diium as donors.

S2. Experimental

An aqueous solution containing 2 mmol of HNO_3 in 10 ml of water was added to 1 mmol of *trans*-2,5-dimethylpiperazine in 20 ml of water. The obtained solution was stirred for 1 h, filtered and then left to stand at room temperature. Colorless single crystals of the title compound were obtained after some days.

S3. Refinement

All H atoms were located in a difference map. Nevertheless, they were geometrically placed and refined using a riding model, with C—H = 0.97 Å (methylene), or 0.96 Å (methyl), or 0.98 Å (methine), N—H = 0.90 Å (NH_2) with $U_{iso}(H)$ = $1.2U_{eq}$(C or N).
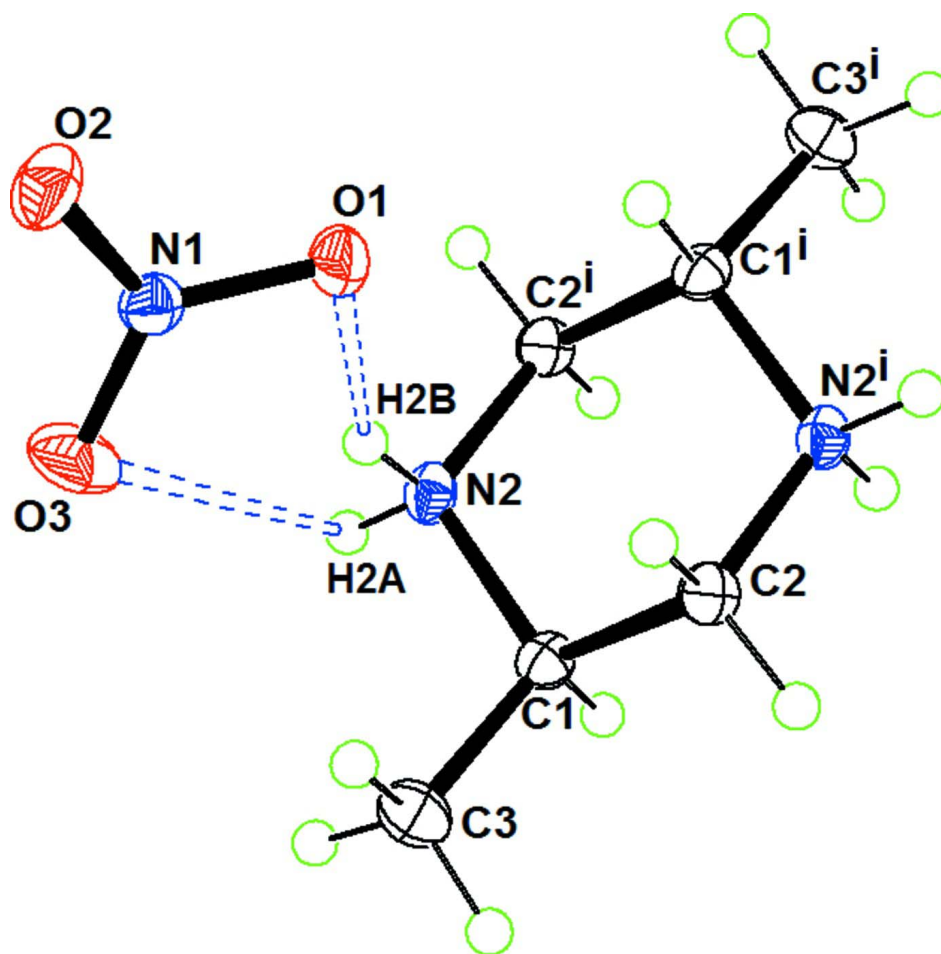
Figure 1

An *ORTEP* view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. Symmetry code: i: -*x*, -*y*, -*z*.
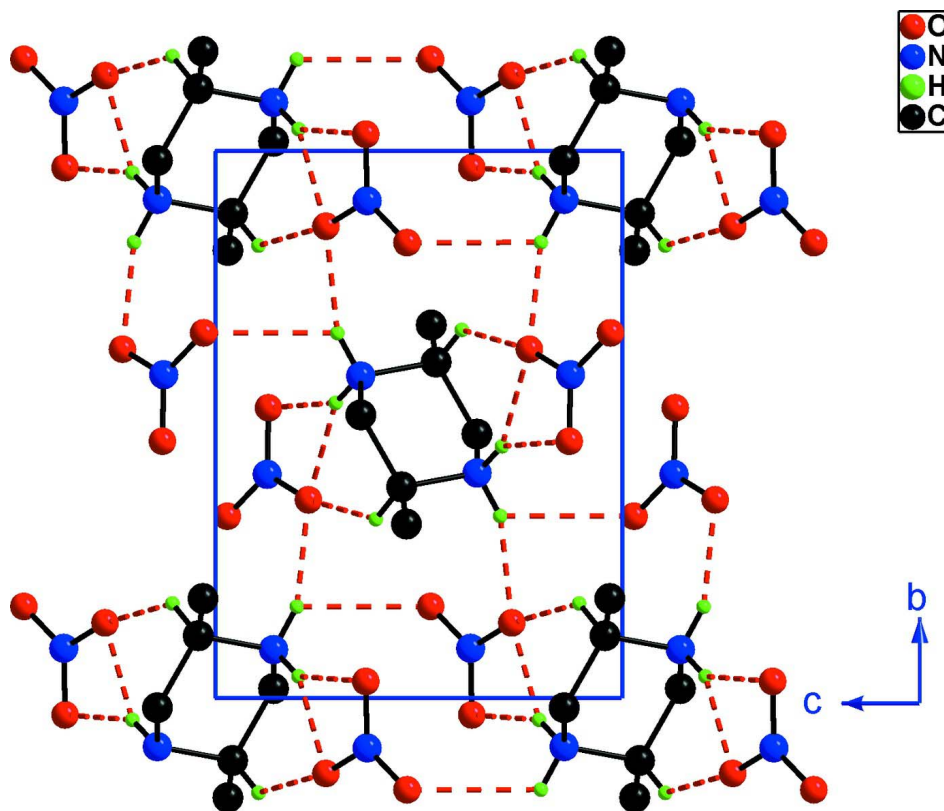
Figure 2

Projection of (I) along the *a* axis. The H-atoms not involved in H-bonding are omitted.

trans-2,5-Dimethylpiperazine-1,4-diium dinitrate

Crystal data

C$_6$H$_{16}$N$_2^{2+}$·2NO$_3^-$

$M_r = 240.23$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.0357$ (8) Å

$b = 10.0277$ (10) Å

$c = 8.3112$ (8) Å

$\beta = 116.149$ (8)°

$V = 526.36$ (9) Å^3

$Z = 2$

$F(000) = 256$

$D_x = 1.516$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2153 reflections

$\theta = 3.4$–27.4°

$\mu = 0.13$ mm^{-1}

$T = 150$ K

Prism, colourless

$0.58 \times 0.46 \times 0.23$ mm

Data collection

Bruker APEXII
    diffractometer

Graphite monochromator

CCD rotation images, thin slices scans

Absorption correction: multi-scan
    (*SADABS*; Bruker, 2006)

$T_{min} = 0.827$, $T_{max} = 0.970$

4126 measured reflections

1195 independent reflections

1059 reflections with $I > 2\sigma(I)$

$R_{int} = 0.022$

$\theta_{max} = 27.5$°, $\theta_{min} = 3.4$°

$h = -8 \rightarrow 9$

$k = -9 \rightarrow 12$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.090$	
$S = 1.11$	H-atom parameters constrained
1195 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.1423P]$ where $P = (F_o^2 + 2F_c^2)/3$
74 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.30$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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}
N1	0.20352 (15)	−0.09103 (10)	−0.37280 (12)	0.0173 (2)
O1	0.12714 (14)	−0.13760 (9)	−0.27150 (11)	0.0218 (2)
O2	0.24377 (15)	−0.16754 (10)	−0.47090 (11)	0.0255 (2)
O3	0.23709 (16)	0.03059 (9)	−0.36962 (13)	0.0312 (3)
N2	−0.02504 (15)	0.08866 (10)	−0.14298 (12)	0.0169 (2)
H2A	−0.0683	0.1671	−0.2001	0.020*
H2B	0.0282	0.0397	−0.2044	0.020*
C1	0.14685 (18)	0.11399 (12)	0.04232 (15)	0.0165 (3)
H1	0.0915	0.1730	0.1057	0.020*
C2	0.21154 (17)	−0.01747 (12)	0.14274 (15)	0.0176 (3)
H2C	0.2778	−0.0736	0.0869	0.021*
H2D	0.3146	−0.0007	0.2653	0.021*
C3	0.33291 (19)	0.18189 (13)	0.03060 (17)	0.0224 (3)
H3A	0.3930	0.1230	−0.0257	0.034*
H3B	0.4381	0.2036	0.1490	0.034*
H3C	0.2854	0.2621	−0.0389	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0184 (5)	0.0158 (5)	0.0155 (5)	0.0005 (4)	0.0054 (4)	0.0005 (4)
O1	0.0288 (5)	0.0212 (5)	0.0202 (4)	−0.0019 (3)	0.0153 (4)	−0.0007 (3)
O2	0.0331 (5)	0.0274 (5)	0.0203 (4)	0.0033 (4)	0.0158 (4)	−0.0025 (4)
O3	0.0356 (5)	0.0134 (5)	0.0400 (6)	−0.0040 (4)	0.0125 (4)	0.0023 (4)
N2	0.0199 (5)	0.0162 (5)	0.0150 (5)	0.0030 (4)	0.0081 (4)	0.0023 (4)

C1	0.0185 (5)	0.0144 (6)	0.0161 (5)	0.0018 (4)	0.0071 (4)	−0.0010 (4)
C2	0.0166 (5)	0.0168 (6)	0.0178 (5)	0.0020 (4)	0.0062 (4)	0.0016 (4)
C3	0.0207 (6)	0.0178 (6)	0.0287 (6)	0.0003 (5)	0.0112 (5)	0.0009 (5)

Geometric parameters (Å, º)

N1—O2	1.2398 (13)	C1—C2	1.5188 (17)
N1—O3	1.2403 (14)	C1—H1	0.9800
N1—O1	1.2706 (13)	C2—N2^i	1.4945 (15)
N2—C2^i	1.4945 (15)	C2—H2C	0.9700
N2—C1	1.5024 (14)	C2—H2D	0.9700
N2—H2A	0.9000	C3—H3A	0.9600
N2—H2B	0.9000	C3—H3B	0.9600
C1—C3	1.5163 (17)	C3—H3C	0.9600
O2—N1—O3	121.73 (10)	C2—C1—H1	108.8
O2—N1—O1	119.62 (10)	N2^i—C2—C1	111.39 (9)
O3—N1—O1	118.65 (10)	N2^i—C2—H2C	109.4
C2^i—N2—C1	112.95 (9)	C1—C2—H2C	109.4
C2^i—N2—H2A	109.0	N2^i—C2—H2D	109.4
C1—N2—H2A	109.0	C1—C2—H2D	109.4
C2^i—N2—H2B	109.0	H2C—C2—H2D	108.0
C1—N2—H2B	109.0	C1—C3—H3A	109.5
H2A—N2—H2B	107.8	C1—C3—H3B	109.5
N2—C1—C3	109.74 (9)	H3A—C3—H3B	109.5
N2—C1—C2	109.11 (9)	C1—C3—H3C	109.5
C3—C1—C2	111.53 (10)	H3A—C3—H3C	109.5
N2—C1—H1	108.8	H3B—C3—H3C	109.5
C3—C1—H1	108.8		

Symmetry code: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1^{ii}	0.90	1.99	2.8471 (14)	158
N2—H2*A*···O2^{iii}	0.90	2.45	2.9899 (13)	119
N2—H2*B*···O1	0.90	2.07	2.9057 (13)	153
N2—H2*B*···O3	0.90	2.42	3.2172 (14)	149
C1—H1···O1^i	0.98	2.50	3.2614 (14)	134

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