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

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Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.022 Å; R factor = 0.033; wR factor = 0.090; data-to-parameter ratio = 16.1.

In the structure of the title salt, C₆H₁₆N₂⁺ ·2NO₃⁻, the cations are connected to the anions through bifurcated N—H···(O) and weak C—H···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

C₆H₁₆N₂²⁺ ·2NO₃⁻
Mᵣ = 240.23
Monoclinic, P₂₁/c
a = 7.0357 (8) Å
b = 10.0277 (10) Å
\( c = 8.3112 (8) Å \)
\( β = 116.149 (8) ° \)
\( V = 526.36 (9) Å³ \)

Z = 2
Mo Kα radiation
μ = 0.13 mm⁻¹

T = 150 K
0.58 × 0.46 × 0.23 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2006)
Tmin = 0.827, Tmax = 0.970

4126 measured reflections
1195 independent reflections
1059 reflections with I > 2σ(I)
Rint = 0.022

Refinement

\( R(F^2) = 0.034 \)
\( wR(F^2) = 0.090 \)
1195 reflections

74 parameters

H-atom parameters constrained
\( Δρ_{max} = 0.30 e Å⁻³ \)
\( Δρ_{min} = −0.23 e Å⁻³ \)

Table 1

Hydrogen-bond geometry (Å, °).

| D···H···A | D···H | H···A | D···A | D···H···A |
|-----------|-------|-------|-------|-----------|
| N2···O2a  | 0.90  | 2.45  | 2.9899 (13) | 119 |
| N2···O2a  | 0.90  | 2.45  | 2.9899 (13) | 119 |
| N2···O1    | 0.90  | 2.07  | 2.9057 (13) | 149 |
| C1···O1iv | 0.98  | 2.50  | 3.2614 (14) | 134 |

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

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

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1. 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, C₆H₁₆N₂(NO₃)₂ (I). The asymmetric unit of (I) is composed of a half trans-2,5-dimethylpiperazine-1,4-diium 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, 2014a,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.

2. Experimental

An aqueous solution containing 2 mmol of HNO₃ 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.

3. 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 (NH₂) with Uiso(H) = 1.2Ueq(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**

$\text{C}_6\text{H}_{16}\text{N}_2^2\cdot2\text{NO}_3^-$

$M_r = 240.23$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.0357 (8)$ Å

$b = 10.0277 (10)$ Å

$c = 8.3112 (8)$ Å

$\beta = 116.149 (8) ^\circ$

$V = 526.36 (9)$ Å$^3$

$Z = 2$

$F(000) = 256$

$D_r = 1.516 \text{ Mg m}^{-3}$

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

Cell parameters from 2153 reflections

$\theta = 3.4$–$27.4^\circ$

$\mu = 0.13$ 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

$(SADABS; \text{Bruker, 2006})$

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

4126 measured reflections

1195 independent reflections

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

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 3.4^\circ$

$h = -8 \rightarrow 9$

$k = -9 \rightarrow 12$

$l = -10 \rightarrow 10$

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Refinement

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

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 (Å²)

|     | 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 (Å²)

|     | 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) |

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supplementary materials

|     |          |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|----------|
| 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, °)

|     |          |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|----------|
| 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—N2i | 1.4945 (15) |
| N2—C2i | 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 |

Symmetry code: (i) −x, −y, −z.

Hydrogen-bond geometry (Å, °)

|     |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|
| O2—N1—O3 | 121.73 (10) | C2—C1—H1 | 108.8 |
| O2—N1—O1 | 119.62 (10) | N2i—C2—C1 | 111.39 (9) |
| O3—N1—O1 | 118.65 (10) | N2i—C2—H2C | 109.4 |
| C2i—N2—C1 | 112.95 (9) | C1—C2—H2C | 109.4 |
| C2i—N2—H2A | 109.0 | N2i—C2—H2D | 109.4 |
| C1—N2—H2A | 109.0 | C1—C2—H2D | 109.4 |
| C2i—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 codes: (i) −x, −y, −z; (ii) −x, y+1/2, −z−1/2; (iii) −x, −y, −z−1.