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1,4-Diazoniabicyclo[2.2.2]octane dinitrate

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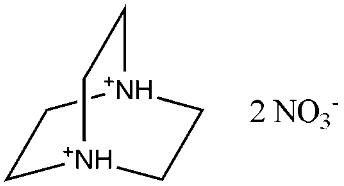
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.156; data-to-parameter ratio = 18.9.

The title compound, $C_6H_{14}N_2^{2+}\cdot 2NO_3^-$, was synthesized under hydrothermal conditions. The asymmetric unit consists of one protonated 1,4-diazabicyclo[2.2.2]octane (DABCO) molecule and two nitrate anions. The structure is stabilized by hydrogen bonding of the nitrate O atoms to the protonated DABCO N atoms, with donor–acceptor distances ranging from 2.729 (2) to 3.111 (2) Å.



Experimental

Crystal data

$C_6H_{14}N_2^{2+}\cdot 2NO_3^-$
M_r = 238.21
Monoclinic, $P2_1/n$
a = 11.4887 (4) Å
b = 6.8821 (2) Å
c = 12.6838 (5) Å
β = 91.247 (5)°
V = 1002.62 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 293 (2) K
0.2 × 0.2 × 0.1 mm

Data collection

Bruker APEX II CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min}$ = 0.972, $T_{\max}$ = 0.986
18932 measured reflections
2891 independent reflections
1701 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.156
S = 1.04
2891 reflections
153 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 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$
N3—H30$\cdots$O4$^{\rm i}$	0.793 (16)	2.009 (16)	2.778 (2)	163 (2)
N3—H30$\cdots$O5$^{\rm i}$	0.793 (16)	2.419 (19)	3.063 (2)	139 (2)
N2—H20$\cdots$O1$^{\rm ii}$	0.832 (15)	1.911 (16)	2.729 (2)	167 (2)
N2—H20$\cdots$O3$^{\rm ii}$	0.832 (15)	2.46 (2)	3.111 (2)	136 (2)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (*CrystalMaker* Software, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the National Science Foundation (grant DMR-0348982, CAREER Award to CLC, and NSF-MRI grant DMR-0419754, diffractometer acquisition), the McConnell Fellowship (KEK) and Sigma Xi Grants in Aid of Research (KEK).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2123).

References

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Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.

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supplementary materials

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1,4-Diazoniabicyclo[2.2.2]octane dinitrate

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Comment

As the field of inorganic organic coordination polymers and metal organic frameworks has developed, it has become increasingly important to explore the oxidation or reduction of organic molecules utlilized in the syntheses of such materials. Consequently the title compound was synthesized as part of an investigation to understand the stability of DABCO under hydrothermal conditions, in the presence of nitrate groups.

Experimental

1,4-Diazabicyclo[2.2.2]octane and concentrated nitric acid were obtained from Sigma-Aldrich. All reagents were used without further purification. 1,4-diazabicyclo[2.2.2]octane (0.098 g, 0.87 mmol) and distilled water (5 g, 278 mmol) were placed into a 23 ml Teflon-lined Parr bomb in the molar ratios of 1.0:320 respectively. The pH was adjusted to 1.5 using concentrated HNO_3. The reaction vessel was then sealed and heated statically at 120 °C for 10 days. Upon cooling to room temperature, a clear colorless solution was obtained. The solvent was allowed to evaporate at room temperature resulting in colourless crystals of the title compound.

Refinement

All H atoms of the DABCO carbons were placed in calculated positions whereas those of the DABCO nitrogen were located in a difference Fourier map. The bond distances to H were fixed at 0.97 Å for the carbon atoms and the H atoms were allowed to ride on their bonded C atoms with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. Those of the nitrogen atoms were freely refined with a distance restraint of 0.8 Å.

Figures

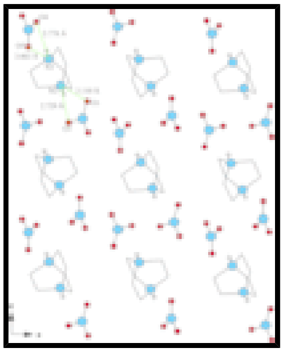

Fig. 1. Packing of the title compound illustrating the hydrogen bonding of the nitrate anion and the protonated DABCO nitrogen.

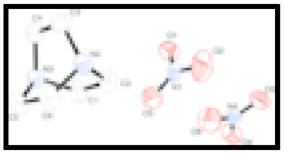

Fig. 2. *ORTEP* drawing of title compound. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

1,4-Diazoniabicyclo[2.2.2]octane dinitrate

Crystal data

$C_6H_{14}N_2^{2+}\cdot 2NO_3^-$

$M_r = 238.21$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 11.4887$ (4) Å

$b = 6.8821$ (2) Å

$c = 12.6838$ (5) Å

$\beta = 91.247$ (5)°

$V = 1002.62$ (6) Å^3

$Z = 4$

$F_{000} = 504$

$D_x = 1.578$ Mg m^{-3}

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

Cell parameters from 2891 reflections

$\theta = 2.4$–30.4°

$\mu = 0.14$ mm^{-1}

$T = 293$ (2) K

Block, colourless

0.2 × 0.2 × 0.1 mm

Data collection

Bruker APEX II CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

ω and φ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2002)

$T_{min} = 0.972$, $T_{max} = 0.986$

18932 measured reflections

2891 independent reflections

1701 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$

$\theta_{max} = 30.4$°

$\theta_{min} = 2.4$°

$h = -16 \rightarrow 16$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.156$

$S = 1.04$

2891 reflections

153 parameters

2 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.2134P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.33$ e Å^{-3}

$\Delta\rho_{min} = -0.21$ e Å^{-3}

Extinction correction: none

Primary atom site location: structure-invariant direct methods

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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.93691 (19)	0.7655 (3)	0.25071 (15)	0.0463 (5)
H1A	0.9694	0.6490	0.2827	0.056*
H1B	0.8701	0.7286	0.2072	0.056*
C2	0.90005 (17)	0.9055 (3)	0.33541 (16)	0.0421 (5)
H2A	0.8164	0.9245	0.3313	0.051*
H2B	0.9200	0.8530	0.4044	0.051*
C3	1.08900 (18)	1.0677 (3)	0.33089 (16)	0.0457 (5)
H3A	1.1094	1.0248	0.4018	0.055*
H3B	1.1280	1.1903	0.3183	0.055*
C4	1.12770 (17)	0.9181 (3)	0.25179 (16)	0.0463 (5)
H4A	1.1883	0.9719	0.2084	0.056*
H4B	1.1588	0.8049	0.2882	0.056*
C5	0.9751 (2)	1.0361 (3)	0.13096 (14)	0.0422 (5)
H5A	0.9122	0.9972	0.0833	0.051*
H5B	1.0342	1.1006	0.0902	0.051*
C6	0.9296 (2)	1.1734 (3)	0.21419 (16)	0.0491 (5)
H6A	0.9641	1.3010	0.2060	0.059*
H6B	0.8458	1.1861	0.2064	0.059*
N1	0.84994 (15)	0.4322 (2)	0.48142 (13)	0.0409 (4)
N2	0.96035 (14)	1.0939 (2)	0.32027 (12)	0.0350 (4)
N3	1.02573 (14)	0.8620 (2)	0.18482 (11)	0.0333 (4)
N4	0.63928 (13)	0.0013 (2)	0.54168 (14)	0.0405 (4)
O1	0.92260 (13)	0.2997 (2)	0.50023 (11)	0.0527 (4)
O2	0.81216 (19)	0.5294 (3)	0.55311 (17)	0.0858 (7)
O3	0.81960 (15)	0.4576 (2)	0.38782 (13)	0.0601 (5)
O4	0.59975 (15)	−0.1572 (2)	0.50989 (12)	0.0583 (5)
O5	0.64042 (15)	0.0298 (3)	0.63862 (13)	0.0630 (5)
O6	0.67368 (18)	0.1223 (3)	0.47992 (16)	0.0897 (7)
H30	1.0467 (19)	0.785 (3)	0.1429 (15)	0.049 (7)*
H20	0.9441 (19)	1.169 (3)	0.3691 (15)	0.051 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0612 (13)	0.0367 (10)	0.0413 (11)	−0.0152 (9)	0.0087 (9)	−0.0028 (9)
C2	0.0408 (11)	0.0442 (11)	0.0418 (10)	−0.0041 (9)	0.0109 (8)	0.0018 (9)
C3	0.0417 (11)	0.0502 (12)	0.0452 (11)	−0.0082 (9)	−0.0008 (8)	−0.0153 (9)
C4	0.0377 (10)	0.0580 (13)	0.0433 (11)	0.0053 (9)	0.0032 (8)	−0.0100 (10)
C5	0.0625 (13)	0.0363 (10)	0.0278 (9)	0.0065 (9)	0.0019 (8)	0.0027 (8)
C6	0.0726 (15)	0.0342 (10)	0.0407 (11)	0.0165 (10)	0.0049 (10)	0.0040 (8)
N1	0.0438 (9)	0.0361 (9)	0.0432 (10)	−0.0021 (7)	0.0114 (7)	−0.0060 (7)
N2	0.0460 (9)	0.0304 (8)	0.0288 (8)	0.0037 (7)	0.0061 (6)	−0.0078 (6)
N3	0.0435 (9)	0.0272 (8)	0.0292 (8)	0.0038 (6)	0.0051 (6)	−0.0065 (6)
N4	0.0344 (8)	0.0420 (9)	0.0448 (9)	−0.0061 (7)	−0.0030 (7)	0.0090 (8)
O1	0.0566 (9)	0.0528 (9)	0.0486 (9)	0.0135 (8)	−0.0027 (7)	−0.0027 (7)
O2	0.0961 (15)	0.0754 (13)	0.0876 (14)	0.0042 (11)	0.0411 (11)	−0.0400 (11)
O3	0.0643 (10)	0.0609 (10)	0.0551 (10)	−0.0022 (8)	−0.0001 (8)	0.0195 (8)
O4	0.0795 (12)	0.0405 (9)	0.0549 (10)	−0.0036 (8)	−0.0013 (8)	−0.0062 (7)
O5	0.0695 (11)	0.0744 (12)	0.0444 (9)	−0.0063 (9)	−0.0102 (7)	−0.0050 (8)
O6	0.0924 (15)	0.0900 (15)	0.0867 (14)	−0.0397 (12)	0.0023 (11)	0.0444 (12)

Geometric parameters (Å, °)

C1—N3	1.489 (2)	C5—C6	1.518 (3)
C1—C2	1.510 (3)	C5—H5A	0.9700
C1—H1A	0.9700	C5—H5B	0.9700
C1—H1B	0.9700	C6—N2	1.488 (3)
C2—N2	1.484 (3)	C6—H6A	0.9700
C2—H2A	0.9700	C6—H6B	0.9700
C2—H2B	0.9700	N1—O2	1.217 (2)
C3—N2	1.492 (3)	N1—O3	1.242 (2)
C3—C4	1.511 (3)	N1—O1	1.255 (2)
C3—H3A	0.9700	N2—H20	0.832 (15)
C3—H3B	0.9700	N3—H30	0.793 (16)
C4—N3	1.483 (3)	N4—O6	1.215 (2)
C4—H4A	0.9700	N4—O5	1.245 (2)
C4—H4B	0.9700	N4—O4	1.245 (2)
C5—N3	1.491 (2)		
N3—C1—C2	108.72 (15)	N3—C5—H5B	110.0
N3—C1—H1A	109.9	C6—C5—H5B	110.0
C2—C1—H1A	109.9	H5A—C5—H5B	108.4
N3—C1—H1B	109.9	N2—C6—C5	108.74 (15)
C2—C1—H1B	109.9	N2—C6—H6A	109.9
H1A—C1—H1B	108.3	C5—C6—H6A	109.9
N2—C2—C1	109.03 (14)	N2—C6—H6B	109.9
N2—C2—H2A	109.9	C5—C6—H6B	109.9
C1—C2—H2A	109.9	H6A—C6—H6B	108.3
N2—C2—H2B	109.9	O2—N1—O3	122.6 (2)

C1—C2—H2B	109.9	O2—N1—O1	120.3 (2)
H2A—C2—H2B	108.3	O3—N1—O1	117.11 (16)
N2—C3—C4	109.12 (15)	C2—N2—C6	109.64 (16)
N2—C3—H3A	109.9	C2—N2—C3	110.30 (15)
C4—C3—H3A	109.9	C6—N2—C3	109.95 (16)
N2—C3—H3B	109.9	C2—N2—H20	109.6 (16)
C4—C3—H3B	109.9	C6—N2—H20	113.0 (16)
H3A—C3—H3B	108.3	C3—N2—H20	104.3 (16)
N3—C4—C3	108.51 (15)	C4—N3—C1	109.69 (15)
N3—C4—H4A	110.0	C4—N3—C5	110.40 (16)
C3—C4—H4A	110.0	C1—N3—C5	110.50 (16)
N3—C4—H4B	110.0	C4—N3—H30	108.1 (16)
C3—C4—H4B	110.0	C1—N3—H30	107.4 (17)
H4A—C4—H4B	108.4	C5—N3—H30	110.7 (16)
N3—C5—C6	108.56 (15)	O6—N4—O5	122.1 (2)
N3—C5—H5A	110.0	O6—N4—O4	120.9 (2)
C6—C5—H5A	110.0	O5—N4—O4	116.99 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H30···O4^{i}	0.793 (16)	2.009 (16)	2.778 (2)	163 (2)
N3—H30···O5^{i}	0.793 (16)	2.419 (19)	3.063 (2)	139 (2)
N2—H20···O1^{ii}	0.832 (15)	1.911 (16)	2.729 (2)	167 (2)
N2—H20···O3^{ii}	0.832 (15)	2.46 (2)	3.111 (2)	136 (2)

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

Fig. 1

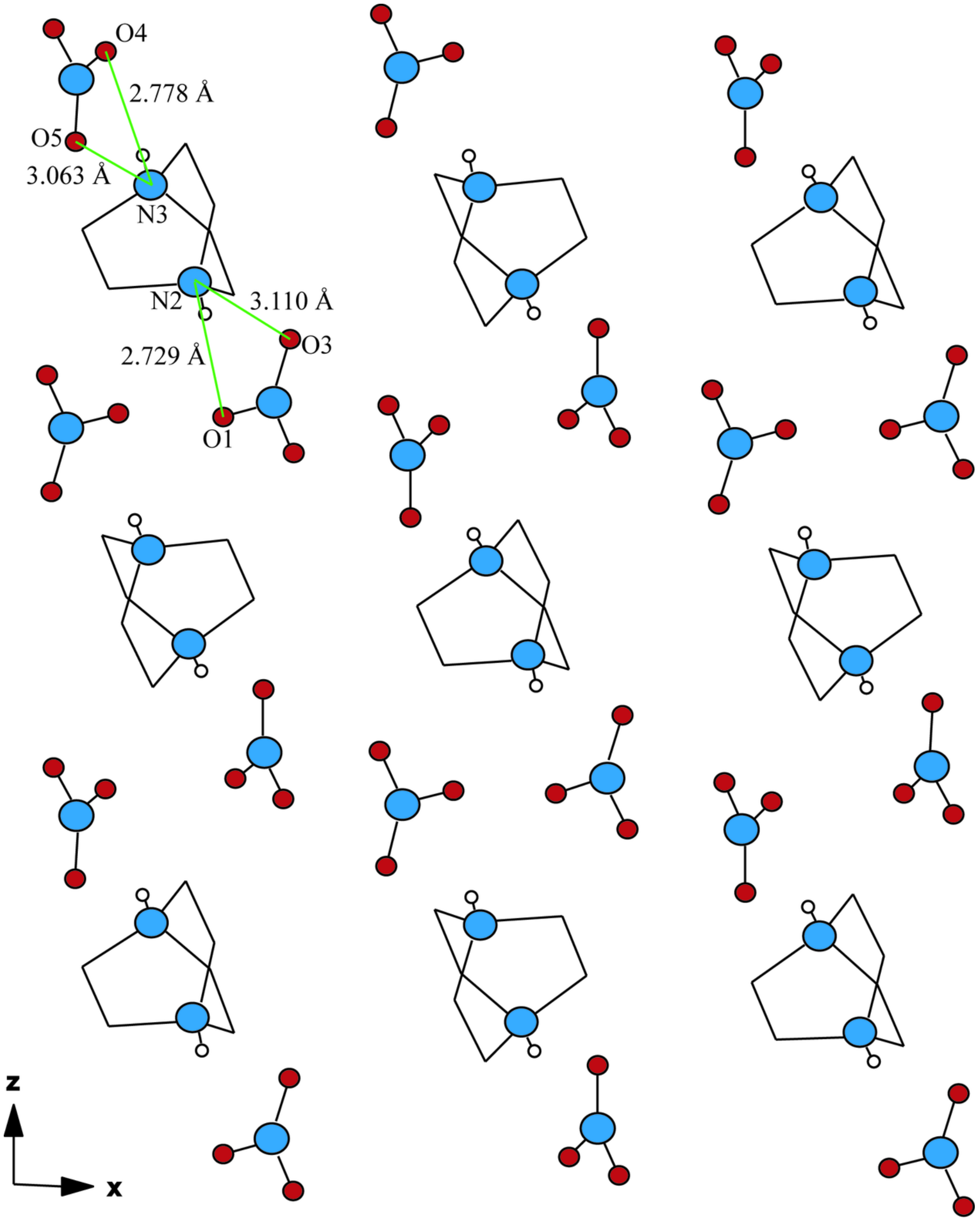

Fig. 2