

3,3-Dinitroazetidinium chloride

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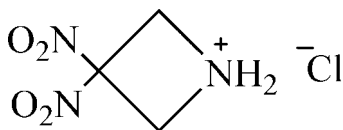
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.021; wR factor = 0.055; data-to-parameter ratio = 11.4.

In the title *gem*-dinitroazetidinium chloride salt, $\text{C}_3\text{H}_6\text{N}_3\text{O}_4^+\text{Cl}^-$, the cations and anions lie on a mirror plane. The azetidine ring is virtually planar, with a mean deviation from the plane of 0.0569 Å. The dihedral angle between the two nitro groups is 90.00 (5)°. In the crystal, the ions are linked by $\text{N}-\text{H}\cdots\text{Cl}$ interactions, forming a chain along the c -axis direction, and $\text{C}-\text{H}\cdots\text{O}$ interactions, forming a layer parallel to (010).

Related literature

For 1,3,3-trinitroazetidine and compounds prepared from its derivative 3,3-dinitroazetidine, see: Archibald *et al.* (1990); Hiskey *et al.* (1992); Ma *et al.* (2009a,b, 2011); Yan *et al.* (2009, 2010); Gao *et al.* (2009). For related structures, see: Gao *et al.* (2010); Ma *et al.* (2010). For the synthesis, see: Li *et al.* (2004).



Experimental

Crystal data

$\text{C}_3\text{H}_6\text{N}_3\text{O}_4^+\text{Cl}^-$
 $M_r = 183.56$
Orthorhombic, $Cmc2_1$
 $a = 6.6807$ (17) Å
 $b = 10.4409$ (17) Å
 $c = 9.9707$ (19) Å
 $V = 695.5$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.52$ mm⁻¹
 $T = 293$ K
0.35 × 0.34 × 0.30 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.839$, $T_{\max} = 0.860$
1968 measured reflections
708 independent reflections
696 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.055$
 $S = 1.10$
708 reflections
62 parameters
1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³
Absolute structure: Flack (1983), 252 Friedel pairs
Flack parameter: 0.09 (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1C}\cdots\text{Cl}^{\text{I}}$	0.90	2.35	3.087 (2)	139
$\text{N1}-\text{H1D}\cdots\text{Cl}^{\text{I}}$	0.90	2.19	3.0575 (19)	163
$\text{Cl}^{\text{I}}-\text{H1B}\cdots\text{O4}^{\text{II}}$	0.97	2.58	3.543 (2)	172

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

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2187).

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supporting information

Acta Cryst. (2012). E68, o3376 [doi:10.1107/S1600536812046302]

3,3-Dinitroazetidinium chloride

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S1. Comment

Dinitro- and trinitro-derivatives of azetidine are of interest because they contain strained ring systems. This makes them good candidates for energetic materials (propellants or explosives). Azetidine-based explosives, such as 1,3,3-trinitroazetidine (TNAZ) (Archibald *et al.*, 1990) demonstrate excellent performance partly because of the high strain associated with the four-membered ring. As one of the important derivatives of TNAZ, 3,3-dinitroazetidine (DNAZ) (Hiskey *et al.*, 1992) can prepare a variety of solid energetic materials with high oxygen-balance (Ma *et al.*, 2009a; Ma *et al.*, 2009b; Yan *et al.*, 2009; Gao *et al.*, 2009; Yan *et al.*, 2010; Ma *et al.*, 2010; Gao *et al.*, 2010; Ma *et al.*, 2011). This paper reports the crystal structure of the title DNAZ salt, $C_3H_6N_3O_4^+.Cl^-$.

In the title dinitroazetidinium chloride salt, cations and anions lie on a mirror plane. The azetidine ring is virtually planar, with a mean deviation from the plane of 0.0569 Å. The dihedral angle between the two nitro groups is 90.00 (5)°. In the crystal, the ions are linked by N—H \cdots Cl and C—H \cdots O interactions.

S2. Experimental

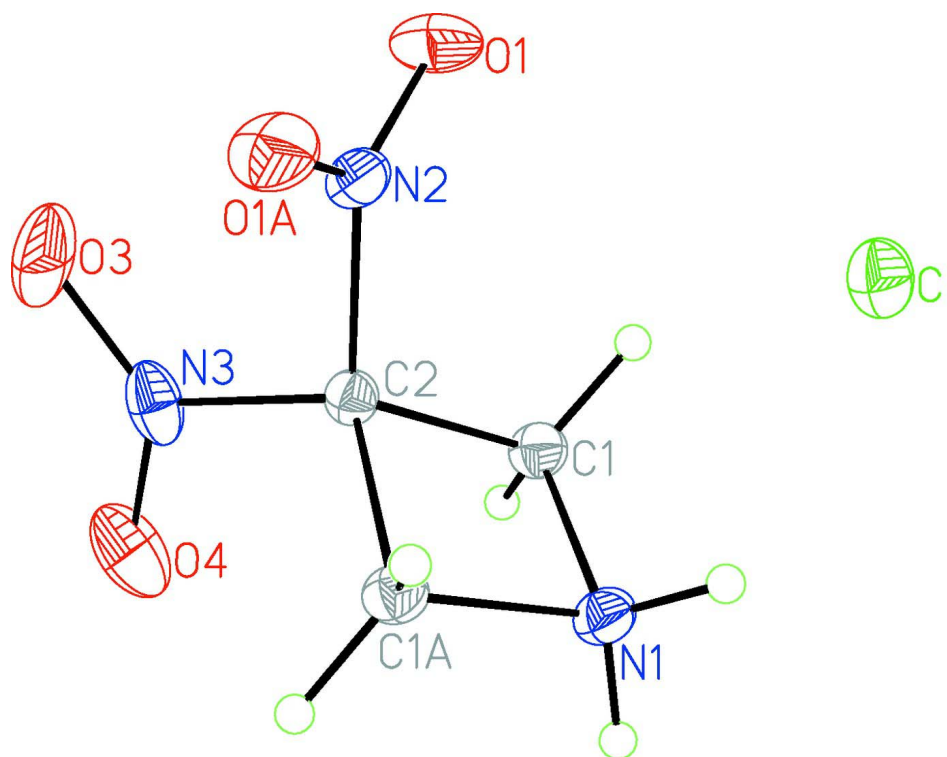
The title compound was synthesized and purified by a reported method (Li *et al.*, 2004). The compound was then dissolved in water and colorless crystals were isolated after 1 d.

Elemental analysis calculated for $C_3H_6N_3O_4Cl$: C 19.63, N 22.89, H 3.29%; found: C 19.74, N 23.10, H 3.19%.

IR (KBr, cm^{-1}): 3057, 2623, 1588, 1406, 1333, 850, 808.

S3. Refinement

H atoms were placed at calculated idealized positions and refined using a riding model, with C—H = 0.97 Å and N—H = 0.90 Å [and $U_{iso}(H) = 1.2U_{eq}(C,N)$].

**Figure 1**

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radius.

3,3-Dinitroazetidinium chloride

Crystal data

$C_3H_6N_3O_4^+ \cdot Cl^-$

$M_r = 183.56$

Orthorhombic, $Cmc2_1$

Hall symbol: $C\ 2c\ -2$

$a = 6.6807\ (17)\ \text{\AA}$

$b = 10.4409\ (17)\ \text{\AA}$

$c = 9.9707\ (19)\ \text{\AA}$

$V = 695.5\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 376$

$D_x = 1.753\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

$\mu = 0.52\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.35 \times 0.34 \times 0.30\ \text{mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ϕ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2000)

$T_{\min} = 0.839$, $T_{\max} = 0.860$

1968 measured reflections

708 independent reflections

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

$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 3.6^\circ$

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 12$

$l = -11 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.055$
 $S = 1.10$
 708 reflections
 62 parameters
 1 restraint
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.199P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.227 (9)
 Absolute structure: Flack (1983), 252 Friedel
 pairs
 Absolute structure parameter: 0.09 (7)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.0000	0.34257 (4)	0.24339 (6)	0.03211 (19)
N2	0.0000	0.14030 (15)	0.5026 (2)	0.0277 (4)
O3	0.0000	0.07128 (19)	0.7449 (3)	0.0571 (6)
C1	0.1613 (2)	0.35120 (12)	0.57848 (17)	0.0255 (3)
H1A	0.2305	0.3773	0.6596	0.031*
H1B	0.2557	0.3293	0.5081	0.031*
N3	0.0000	0.1881 (2)	0.7388 (3)	0.0354 (4)
N1	0.0000	0.44299 (15)	0.5346 (2)	0.0269 (4)
H1C	0.0000	0.4581	0.4457	0.032*
H1D	0.0000	0.5170	0.5808	0.032*
O4	0.0000	0.2614 (3)	0.8318 (2)	0.0536 (6)
O1	0.16253 (18)	0.10036 (10)	0.46749 (16)	0.0425 (4)
C2	0.0000	0.24966 (18)	0.6017 (2)	0.0217 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0359 (3)	0.0347 (3)	0.0258 (3)	0.000	0.000	0.0048 (3)
N2	0.0314 (9)	0.0207 (8)	0.0309 (11)	0.000	0.000	0.0002 (7)
O3	0.0562 (12)	0.0522 (10)	0.0629 (14)	0.000	0.000	0.0373 (12)
C1	0.0226 (7)	0.0236 (7)	0.0304 (8)	-0.0015 (5)	0.0008 (6)	-0.0013 (5)
N3	0.0232 (8)	0.0556 (11)	0.0273 (9)	0.000	0.000	0.0133 (13)

N1	0.0323 (10)	0.0202 (7)	0.0283 (9)	0.000	0.000	-0.0012 (7)
O4	0.0463 (12)	0.0904 (16)	0.0240 (9)	0.000	0.000	-0.0017 (9)
O1	0.0365 (7)	0.0362 (6)	0.0549 (9)	0.0117 (4)	-0.0002 (7)	-0.0136 (6)
C2	0.0218 (9)	0.0215 (9)	0.0217 (11)	0.000	0.000	0.0007 (7)

Geometric parameters (Å, °)

N2—O1 ⁱ	1.2147 (14)	C1—H1B	0.9700
N2—O1	1.2147 (14)	N3—O4	1.203 (4)
N2—C2	1.510 (3)	N3—C2	1.511 (3)
O3—N3	1.221 (3)	N1—C1 ⁱ	1.5073 (19)
C1—N1	1.5073 (18)	N1—H1C	0.9000
C1—C2	1.5294 (19)	N1—H1D	0.9000
C1—H1A	0.9700	C2—C1 ⁱ	1.5294 (19)
O1 ⁱ —N2—O1	126.74 (19)	O4—N3—C2	115.2 (2)
O1 ⁱ —N2—C2	116.63 (9)	O3—N3—C2	118.0 (3)
O1—N2—C2	116.63 (9)	C1—N1—C1 ⁱ	91.30 (15)
N1—C1—C2	88.89 (11)	C1—N1—H1C	113.4
N1—C1—H1A	113.8	C1—N1—H1D	113.4
C2—C1—H1A	113.8	H1C—N1—H1D	110.7
N1—C1—H1B	113.8	N2—C2—N3	105.67 (17)
C2—C1—H1B	113.8	N2—C2—C1	115.17 (13)
H1A—C1—H1B	111.1	N3—C2—C1	115.58 (13)
O4—N3—O3	126.7 (3)	C1—C2—C1 ⁱ	89.62 (15)
C2—C1—N1—C1 ⁱ	8.66 (17)	O3—N3—C2—N2	0.0
O1 ⁱ —N2—C2—N3	89.58 (16)	O4—N3—C2—C1	51.39 (11)
O1—N2—C2—N3	-89.58 (16)	O3—N3—C2—C1	-128.61 (11)
O1 ⁱ —N2—C2—C1	-141.56 (16)	O4—N3—C2—C1 ⁱ	-51.39 (11)
O1—N2—C2—C1	39.3 (2)	O3—N3—C2—C1 ⁱ	128.61 (11)
O1 ⁱ —N2—C2—C1 ⁱ	-39.3 (2)	N1—C1—C2—N2	109.30 (15)
O1—N2—C2—C1 ⁱ	141.56 (16)	N1—C1—C2—N3	-126.93 (15)
O4—N3—C2—N2	180.0	N1—C1—C2—C1 ⁱ	-8.53 (17)

Symmetry code: (i) $-x, y, z$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1C \cdots Cl	0.90	2.35	3.087 (2)	139
N1—H1D \cdots Cl ⁱⁱ	0.90	2.19	3.0575 (19)	163
C1—H1B \cdots O1	0.97	2.50	2.8432 (19)	100
C1—H1B \cdots O4 ⁱⁱⁱ	0.97	2.58	3.543 (2)	172

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