Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O1*B*	0.82	1.89	2.675 (2)	160
O1*B*—H1*B*···O1*C*	0.82	1.90	2.673 (2)	157
O1*C*—H1*C*···O1*D*	0.82	1.89	2.708 (2)	174
O1*D*—H1*D*···O1*A*	0.82	1.88	2.683 (2)	165
O1*A*—H2*A*···O1*D*	0.82	1.88	2.683 (2)	167
O1*B*—H2*B*···O1*A*	0.82	1.93	2.675 (2)	151
O1*C*—H2*C*···O1*B*	0.82	1.88	2.673 (2)	164
O1*D*—H2*D*···O1*C*	0.82	1.91	2.708 (2)	166

$\Delta\rho$ maps computed in the plane of the phenolic O atoms showed that the phenolic H atoms were disordered equally over two sites; this was allowed for in the *SHELXL*93 refinement (Sheldrick, 1993). Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM CAD*-4/*PC*. Data reduction: *DATRD*2 (*NRCVAX*94; Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94, *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek, 1995*b*) . Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*96.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1366). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(hydrazinium) *N*,*N'*-Dinitroethylenediaminate(2−)

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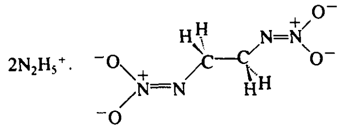
Abstract

The title compound, $2N_2H_5^+.C_2H_2N_4O_4^{2-}$, is an inherently insensitive high-energy material. The anion has C_i symmetry and is almost planar. The nitrate groups are asymmetric, with a mean nitrate N—O distance longer than that found in *N*,*N'*-dinitroethylenediamine and an N1—N2 distance close to a double-bond value.

Comment

Explosives are compounds or mixtures of compounds with a high potential energy. They release large amounts of hot gases in a fast exothermic reaction. One of the main tasks in the chemistry of high-energy materials is the synthesis of molecules with a high activation barrier to energy release (Schubert, 1993; Becuwe & Delclos, 1993; Atkins, Nielsen, Hollis & Willer, 1983). In this context, we have synthesized the title compound, (I), which is extremely insensitive to impact and fairly insensitive to friction.



(I)

The dinitroethylenediaminate dianion (Fig. 1) of (I) is located on an inversion center. The nitroaminate group is planar and the molecule as a whole is almost planar. Atom C1 deviates by 0.024 (2) Å from the best plane through atoms N1, N2, O1 and O2. The C1'—C1—N1—N2 torsion angle is −178.00 (7)°. This is in contrast to *N*,*N'*-dinitroethylenediamine (DNEDAM; Turley, 1967) which also has an almost planar CH_2NHNO_2 group, but whose C1'—C1—N1—N2 torsion angle is 83.8 (4)°. The N1—N2 distance of 1.273 (1) Å is close to a double-bond distance and shorter than that found in DNEDAM [1.301 (4) Å]. The mean nitrate N—O distance of 1.283 (1) Å is longer than that found

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in DNEDAM [1.238 (5) Å]. The distances and angles of the nitrate group are asymmetric: N2—O1 1.294 (1) Å and N1—N2—O1 118.48 (7)° against N2—O2 1.271 (1) Å and N1—N2—O2 123.65 (7)°. The longer N—O bond is opposite the larger N—N—O angle. This asymmetry corresponds to the asymmetry in the hydrogen-bonding pattern of the O atoms; O1 with the longer N—O distance participates in more hydrogen bonds [O1···H3 1.95 (2), O1···H6 2.32 (2), O1···H7 2.42 (2) and O1···H4 2.55 (1) Å] than the O2 atom [O2···H4 1.91 (1) Å] (Table 3). A similar pattern is also found in both tetraaqua(*N*,*N*′-ethylenedinitroaminato-*N*,*N*′)nickel(II) (Palopoli, Geib, Rheingold & Brill, 1988) and disodium *N*,*N*′-dinitroethylenediaminate (NAETNA; Allentoff & Wright, 1953).

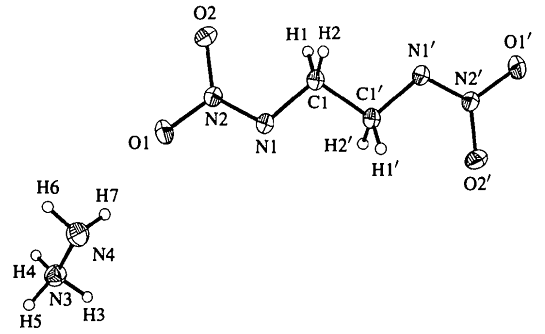

Fig. 1. The molecular structure of title compound showing the atomic numbering and 50% probability displacement ellipsoids.

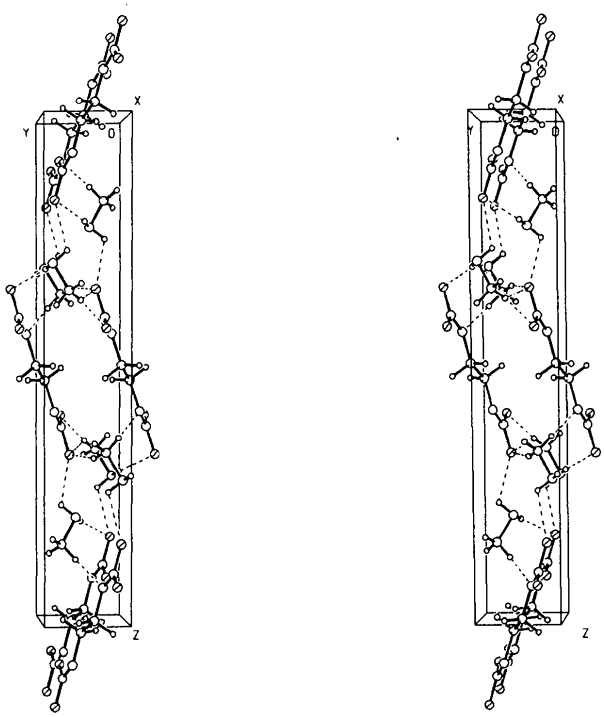

Fig. 2. The packing diagram of the title compound with hydrogen bonds shown as dashed lines. The *z* axis is vertical and the *y* axis is horizontal.

The packing of the dianion in the title compound (Fig. 2) shows a herringbone motif, with stacks of parallel dinitroethylenediaminate dianions parallel to the *b* axis at the cell edges and stacks in the middle of the cell related by the 2_1 axis. The molecular planes make an angle of 69.4° with the *b* axis and have a plane-to-plane distance of 3.61 Å. The molecules in the stacks are linked through hydrazinium ions by a three-dimensional network of hydrogen bonds [O2···H4—N3 1.91 (1), O1···H3—N3 1.95 (2), N1···H5—N3 2.03 (2), O1···H6—N4 2.32 (2), O1···H7—N4 2.42 (2) and O1···H4—N3 2.55 (1) Å].

NAETNA and the title compound have almost the same packing pattern, with sodium taking the place of the hydrazinium ion. The longest cell axis of the latter is 3.54 Å longer than that of NAETNA; this results from the larger space requirements of the hydrazinium molecules.

Experimental

The title compound was prepared by a two-step synthesis starting with nitration of imidazolidone (Urbanski, 1985) and followed by hydrolysis in an aqueous solution of hydrazine.

Crystal data

$2N_2H_5^+.C_2H_2N_4O_4^{2-}$
$M_r = 212.22$
Monoclinic
$P2_1/n$
$a = 5.432\,(1)$ Å
$b = 3.769\,(1)$ Å
$c = 21.959\,(4)$ Å
$\beta = 95.66\,(3)°$
$V = 447.4\,(2)$ Å^3
$Z = 2$
$D_x = 1.590$ Mg m^{-3}
$D_m = 1.594$ Mg m^{-3}
D_m measured by pycnometry in hexane

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 9.3–14.2°$
$\mu = 0.142$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.45 × 0.4 × 0.38 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3059 measured reflections
1606 independent reflections
1240 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0242$
$\theta_{\rm max} = 32.46°$
$h = -8 \rightarrow 8$
$k = -5 \rightarrow 5$
$l = 0 \rightarrow 33$
3 standard reflections frequency: 60 min intensity decay: 10.0%

Refinement

Refinement on F^2
$R(F) = 0.0318$
$wR(F^2) = 0.1006$
$S = 1.034$
1583 reflections
93 parameters

$\Delta\rho_{\rm max} = 0.34$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.127 (14)

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 0.0403P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.61351 (14)	0.0622 (2)	0.48545 (3)	0.0210 (2)
N1	0.53110 (13)	0.1687 (2)	0.42285 (3)	0.0224 (2)
N2	0.70608 (12)	0.2697 (2)	0.39243 (3)	0.0202 (2)
O1	0.65279 (12)	0.3642 (2)	0.33602 (3)	0.0320 (2)
O2	0.93140 (11)	0.2820 (2)	0.41425 (3)	0.0318 (2)
N4	0.4160 (2)	0.4111 (3)	0.21075 (4)	0.0286 (2)
N3	0.29882 (14)	0.2325 (2)	0.15746 (4)	0.0241 (2)
H1	0.737 (3)	−0.123 (4)	0.4865 (6)	0.033 (3)
H2	0.694 (3)	0.263 (4)	0.5103 (7)	0.032 (3)
H3	0.165 (3)	0.110 (5)	0.1693 (7)	0.042 (4)
H4	0.407 (3)	0.090 (4)	0.1386 (6)	0.035 (3)
H5	0.231 (3)	0.389 (5)	0.1287 (8)	0.055 (5)
H6	0.560 (3)	0.483 (5)	0.2009 (7)	0.051 (4)
H7	0.449 (3)	0.240 (5)	0.2352 (9)	0.057 (5)

Table 2. *Selected geometric parameters (Å, °)*

C1—N1	1.459 (1)	N4—N3	1.443 (1)
C1—H1	0.97 (1)	N4—H6	0.87 (2)
C1—H2	1.01 (1)	N4—H7	0.85 (2)
C1—C1$^{\rm i}$	1.518 (1)	N3—H3	0.92 (2)
N1—N2	1.273 (1)	N3—H4	0.92 (1)
N2—O1	1.294 (1)	N3—H5	0.91 (2)
N2—O2	1.271 (1)		
N1—C1—H1	111.6 (8)	N3—N4—H6	106 (1)
N1—C1—H2	112.3 (8)	N3—N4—H7	102 (1)
N1—C1—C1$^{\rm i}$	107.16 (6)	H6—N4—H7	105 (2)
H1—C1—H2	106 (1)	N4—N3—H3	107.6 (9)
H1—C1—C1$^{\rm i}$	110.9 (9)	N4—N3—H4	112.8 (8)
H2—C1—C1$^{\rm i}$	109.4 (9)	N4—N3—H5	112 (1)
C1—N1—N2	113.64 (6)	H3—N3—H4	113 (1)
N1—N2—O1	118.48 (7)	H3—N3—H5	104 (1)
N1—N2—O2	123.65 (7)	H4—N3—H5	107 (1)
O1—N2—O2	117.85 (7)		
H1—C1—N1—N2	−56.4 (9)	H6—N4—N3—H4	42 (2)
H2—C1—N1—N2	61.9 (9)	H6—N4—N3—H5	−79 (2)
C1$^{\rm i}$—C1—N1—N2	−178.00 (7)	H7—N4—N3—H3	58 (2)
C1—N1—N2—O1	178.90 (7)	H7—N4—N3—H4	−68 (2)
C1—N1—N2—O2	−0.9 (1)	H7—N4—N3—H5	172 (2)
H6—N4—N3—H3	167 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 3. *Contact distances (Å)*

N1···H5$^{\rm i}$	2.03 (2)	O1···H7	2.42 (2)
O1···H3$^{\rm ii}$	1.95 (2)	O1···H4$^{\rm iv}$	2.55 (1)
O1···H6$^{\rm iii}$	2.32 (2)	O2···H4$^{\rm iv}$	1.91 (1)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA* (Dreissig, Doherty, Stewart & Hall, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(4,6-Dichloro-1,3,5-triazin-2-ylethynyl)-dimethylamine

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Abstract

The title compound, $C_7H_6Cl_2N_4$, is a push–pull acetylene. The minimum distance between the centers of triple bonds of 5.27 (3) Å is unsuitably long for solid-state

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