$C_8H_9N_3O_4$

Grandjean, Dudragne & Michaud (1976); (*j*) Prasad, Gabe & Le Page (1982); (*k*) Korp, Bernal & Martin (1981). * 1-pyrazole. † C_6H_{11} = cyclohexyl.

Examination of the structure with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: *CAD-4/PC* (Enraf–Nonius, 1992); *MAD-NES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *CAD-4/PC*; *MADNES*. Data reduction: *CAD-4/PC*; *MADNES*; *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *NRC-VAX94*; *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*; *ORTEP*II (Johnson, 1976) in *PLATON* (Spek, 1994*a*); *PLUTON* (Spek, 1994*b*). Software used to prepare material for publication: *NRCVAX94*; *SHELXL93*.

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Energetic Materials: the Biguanidium Nitrates

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Abstract

The structures of two new potentially energetic biguanidium salts, biguanidium nitrate, $C_2H_8N_5^+.NO_3^-$ [(BIGH)NO$_3$], and biguanidium dinitrate, $C_2H_9N_5^{2+}.2NO_3^-$ [(BIGH$_2$)(NO$_3$)$_2$], have been determined from X-ray data collected at 193 K. The mono- and diprotonated biguanidium nitrates are dense organic materials with efficient packing of planar anions and biplanar (twisted) cations connected by multiple hydrogen bonds. The experimental densities are compared with those obtained from empirical calculations.
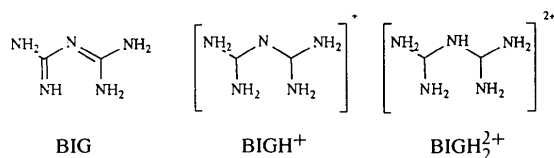
Comment

There is current interest (Borman, 1994) in the development of new energetic materials (such as explosives or propellants) and in understanding the properties of these materials, particularly with respect to their structures (Olah & Squire, 1991). One class of compounds that have solicited interest are derived from guanidinium nitrate (GN) and include, for example, diaminoguanidinium nitrate (DAGN) (Ritchie, Lee, Cromer, Kober & Lee, 1990) and triaminoguanidinium nitrate (TAGN) (Bracuti, 1979; Choi & Prince, 1979; Oyumi & Brill, 1985).

GN   DAGN   TAGN
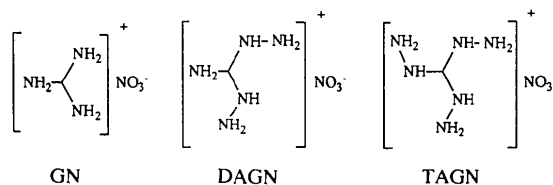
The utility of these compounds in the field of energetic materials is derived from their rapid thermal decomposition into all-gaseous products (Oyumi & Brill, 1985, and references therein). The effectiveness of materials as either explosives or propellants is related to the density of the solid, the gas volume produced and the heat of combustion (Gilardi & Karle, 1991). DAGN and TAGN have useful properties as propellants, their densities being fairly high for organic materials (1.61 and 1.59 Mg m^{-3} for DAGN and TAGN, respectively). Our

previous experience with biguanidium salts (Pinkerton & Schwarzenbach, 1978) suggested that these closely related cations might be used to prepare higher density nitrates.

Empirical calculations (Chichra, Holden & Dickinson, 1980; Stine, 1981; hereafter CHD and ST, respectively) for the monoprotonated and diprotonated biguanidium nitrates (BIGH)NO$_3$ and (BIGH$_2$)(NO$_3$)$_2$, using appropriate atomic volumes, predicted densities of 1.63 (CHD) or 1.61 Mg m^{-3} (ST) for (BIGH)NO$_3$ and 1.77 (CHD) or 1.74 Mg m^{-3} (ST) for (BIGH$_2$)(NO$_3$)$_2$. Analogous calculations gave 1.74 (CHD) or 1.68 Mg m^{-3} (ST) for DAGN, and 1.75 (CHD) or 1.68 Mg m^{-3} for TAGN. We note that the observed densities for DAGN and TAGN are somewhat less than the calculated densities, and that the value predicted for (BIGH$_2$)(NO$_3$)$_2$ is the highest of the four compounds. We have thus synthesized and characterized both the monoprotonated and diprotonated biguanidium nitrates and report our results herein.

Fig. 1. The BIGH$^+$ cation showing the atom-numbering and hydrogen-bonding schemes (50% probability ellipsoids). [Symmetry codes: (a) $x + 1$, y, z; (b) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (c) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (d) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (e) $-x$, $-y$, $-z$.]

BIG   BIGH$^+$ BIGH$_2^{2+}$

The structures of the delocalized cations (Figs. 1 and 2) are very similar to those previously reported for the chloride BIGH.Cl (Ernst, 1977), the carbonate (BIGH)$_2$CO$_3$ and the sulfates (BIGH)$_2$SO$_4$.2H$_2$O and (BIGH$_2$)SO$_4$.H$_2$O (Pinkerton & Schwarzenbach, 1978). Both cations are composed of two planar halves with one atom in common. The two halves are twisted with respect to each other due to the intramolecular H$\cdots$H interaction [BIGH$^+$ 37.8 (1)°; BIGH$_2^{2+}$ 47.0 (1)°]. All bonds are short due to extensive π delocalization, producing bond orders greater than one. As previously noted, protonation of the bridge N atom leads to a small increase in the C—N bridge bond lengths (compared to the monoprotonated cation) with a concomitant shortening of the terminal C—N bonds.

Both crystal structures are characterized by an extensive hydrogen-bonding network. The packing diagram for (BIGH)NO$_3$ (Fig. 3) shows that there are layers of strongly hydrogen-bonded cations and anions. The layers are then connected by one additional hydrogen bond. The biguanidium cations form hydrogen-bonded dimers (Fig. 1) across an inversion center with the bridge N atom acting as the acceptor. It can also be seen from this diagram that all but two of the H atoms (H2*B* and H4*A*) take part in hydrogen bonding. However, H2*B* forms a square arrangement with O3 across a center of symmetry with rather longer contact distances [the sides of the 'square' are 2.43 (2) and 2.52 (2) Å, with angles at O and H of 86.5 (5) and 93.6 (6)°, respectively]. Here, the
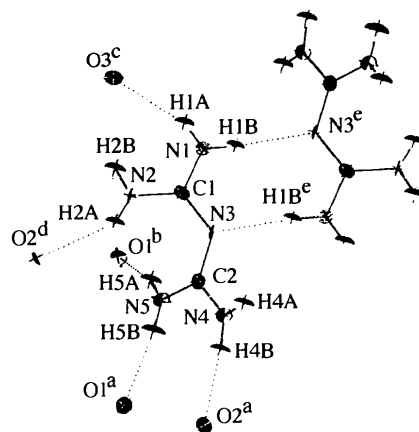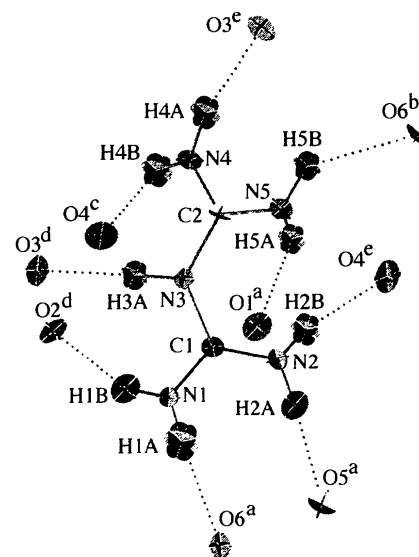

Fig. 2. The BIGH$_2^{2+}$ cation showing the atom-numbering and hydrogen-bonding schemes (50% probability ellipsoids). [Symmetry codes: (a) $x + \frac{1}{2}$, $-y + 2$, z; (b) $-x + 1$, $-y + 1$, $z + \frac{1}{2}$; (c) $-x + 1$, $-y + 1$, $z - \frac{1}{2}$; (d) $-x + \frac{1}{2}$, y, $z - \frac{1}{2}$; (e) $x + \frac{1}{2}$, $-y + 1$, z.]

competing O atoms seem to force H2*B* into a less favorable position. It would appear that the putative square is distorted by the additional hydrogen bonds to the nitrate groups. The nitrate anion is unremarkable and accepts five hydrogen bonds.

The diprotonated biguanidium cation in (BIGH$_2$)-(NO$_3$)$_2$ has a hydrogen bond from every H atom to a nitrate O atom (Fig. 2). The nitrate groups have the expected geometry, and every O atom accepts at least one hydrogen bond. The hydrogen-bonding scheme for (BIGH$_2$)(NO$_3$)$_2$ is now truly three-dimensional (Fig.
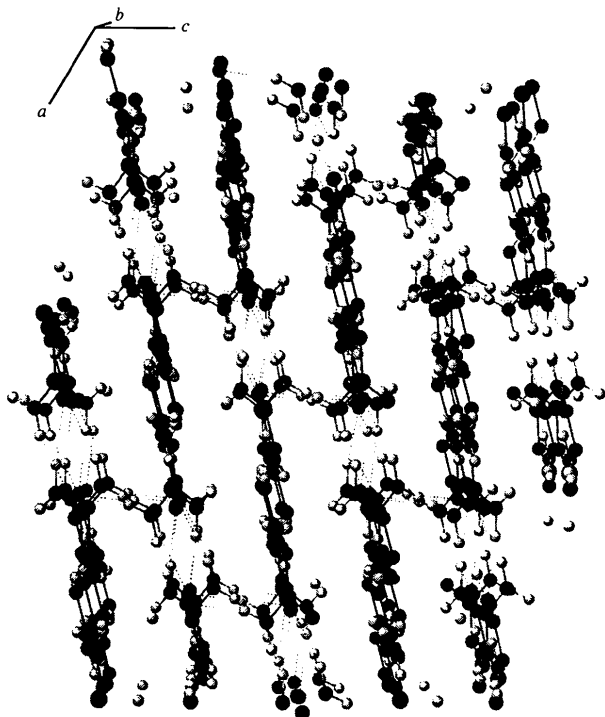
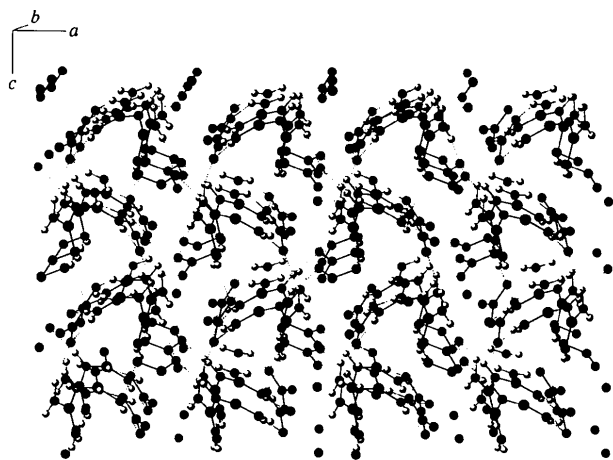Fig. 3. Packing diagram for (BIGH)NO₃ showing the hydrogen bonding and layer structure.

Fig. 4. Packing diagram for (BIGH₂)(NO₃)₂ showing the three-dimensional hydrogen-bonding scheme.

4) and, for this reason, the packing diagram is less informative because there are no obvious viewing directions. It is worth noting, however, that the H atom on the bridging N atom (H3A) forms a particularly strong hydrogen bond [O···H 1.83 (3) Å].

The crystals of both compounds are very compact, as evidenced by their densities [(BIGH)NO₃ 1.62 (193 K), 1.59 Mg m⁻³ (298 K); (BIGH₂)(NO₃)₂ 1.75 (193 K),

1.73 Mg m⁻³ (298 K)], which are very close to the values predicted above. Indeed, both compounds have higher densities than either DAGN or TAGN, which would not have been predicted. It is tempting to ascribe this to more efficient packing or more favorable hydrogen bonding; however, the evidence is weak. It has been noted that density predictions for energetic-material salts tend to be less reliable than for neutral energetic molecules (Gilardi, 1994).
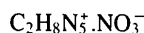
It is thus demonstrated that the protonated biguanidium species are good cations for preparing high-density solids with flat anions capable of accepting hydrogen bonds.

Experimental

(BIGH)NO₃ was prepared easily from aqueous solutions of biguanidium sulfate and barium nitrate followed by filtration and slow evaporation. (BIGH₂)(NO₃)₂ was prepared by acidifying the above solution with nitric acid, followed by slow evaporation.

(BIGH)NO₃

Crystal data

$C_2H_8N_5^+.NO_3^-$	Mo $K\alpha$ radiation
$M_r = 164.12$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 6.959 (1)$ Å	$\theta = 9-15°$
$b = 10.778 (2)$ Å	$\mu = 0.136$ mm⁻¹
$c = 9.489 (2)$ Å	$T = 193$ K
$\beta = 109.28 (2)°$	Prism
$V = 671.8 (4)$ Å³	$0.40 \times 0.21 \times 0.19$ mm
$Z = 4$	Colorless
$D_x = 1.62$ Mg m⁻³	

Data collection

Enraf–Nonius CAD-4	1321 observed reflections
diffractometer	$[I > 3\sigma(I)]$
ω scans	$R_{int} = 0.022$
Absorption correction:	$\theta_{max} = 25.97°$
ψ scans (North, Phillips	$h = 0 \rightarrow 8$
& Mathews, 1968)	$k = 0 \rightarrow 13$
$T_{min} = 0.848$, $T_{max} =$	$l = -11 \rightarrow 11$
0.998	3 standard reflections
1518 measured reflections	frequency: 50 min
1403 independent reflections	intensity decay: 0.01%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.046$	$\Delta\rho_{max} = 0.301$ e Å⁻³
$wR = 0.048$	$\Delta\rho_{min} = -0.354$ e Å⁻³
$S = 1.420$	Extinction correction: none
1321 reflections	Atomic scattering factors
132 parameters	from *International Tables*
All H-atom parameters	*for X-ray Crystallography*
refined	(1974, Vol. IV)
$w = 4F_o^2/[\sigma^2(F_o^2)$	
$+ 0.0016F_o^4]$	

(BIGH₂)(NO₃)₂

Crystal data

$C_2H_9N_5^{2+}.2NO_3^-$
$M_r = 227.14$
Orthorhombic
$Pca2_1$
$a = 14.0232\ (8)$ Å
$b = 6.8842\ (5)$ Å
$c = 8.9541\ (5)$ Å
$V = 864.4\ (2)$ Å³
$Z = 4$
$D_x = 1.75$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections
$\theta = 10\text{--}14°$
$\mu = 0.157$ mm⁻¹
$T = 193$ K
Prism
$0.35 \times 0.22 \times 0.19$ mm
Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips
  & Mathews, 1968)
  $T_{min} = 0.949$, $T_{max} = 0.998$
1026 measured reflections
1026 independent reflections

841 observed reflections
$[I > 3\sigma(I)]$
$\theta_{max} = 25.97°$
$h = -8 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 0$
3 standard reflections
frequency: 50 min
intensity decay: 0.22%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.037$
$S = 0.854$
841 reflections
172 parameters
All H-atom parameters
refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0064F_o^4]$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.181$ e Å⁻³
$\Delta\rho_{min} = -0.205$ e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$) for (BIGH)NO₃*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{eq}/U_{iso}
O1	−0.0128 (2)	0.18355 (9)	0.3222 (1)	0.0308 (3)
O2	−0.0235 (1)	−0.01718 (9)	0.3236 (1)	0.0299 (3)
O3	0.2577 (1)	0.07882 (9)	0.4369 (1)	0.0299 (3)
N1	−0.0627 (2)	0.1670 (1)	−0.0557 (1)	0.0253 (3)
N2	0.1916 (2)	0.3048 (1)	0.0504 (1)	0.0280 (3)
N3	0.2420 (2)	0.0877 (1)	0.0852 (1)	0.0224 (3)
N4	0.5335 (2)	0.0045 (1)	0.2425 (1)	0.0282 (3)
N5	0.5651 (2)	0.1690 (1)	0.1024 (1)	0.0282 (3)
N6	0.0741 (2)	0.0813 (1)	0.3608 (1)	0.0215 (3)
C1	0.1288 (2)	0.1874 (1)	0.0262 (1)	0.0200 (3)
C2	0.4448 (2)	0.0902 (1)	0.1419 (1)	0.0204 (3)
H1A	−0.138 (2)	0.227 (2)	−0.074 (2)	0.031 (4)
H1B	−0.106 (2)	0.092 (1)	−0.067 (2)	0.026 (4)
H2A	0.310 (2)	0.323 (1)	0.102 (2)	0.028 (4)
H2B	0.112 (2)	0.361 (2)	−0.003 (2)	0.035 (4)
H4A	0.460 (2)	−0.036 (2)	0.275 (2)	0.032 (4)
H4B	0.668 (2)	−0.008 (2)	0.274 (2)	0.031 (4)
H5A	0.515 (2)	0.211 (2)	0.018 (2)	0.037 (5)
H5B	0.694 (3)	0.167 (2)	0.151 (2)	0.046 (5)

Table 2. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$) for (BIGH₂)(NO₃)₂*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{eq}/U_{iso}
O1	0.1254 (1)	0.9811 (2)	0.9719	0.0265 (3)
O2	0.0079 (1)	1.0753 (2)	1.1095 (2)	0.0246 (3)
O3	−0.00228 (9)	0.8047 (2)	0.9843 (2)	0.0262 (3)
O4	0.3722 (1)	0.5305 (2)	0.9179 (2)	0.0335 (4)
O5	0.3972 (1)	0.8212 (2)	0.8372 (2)	0.0381 (4)
O6	0.3126 (1)	0.6208 (2)	0.7072 (2)	0.0270 (3)
N1	0.6960 (1)	1.0265 (2)	0.6430 (2)	0.0205 (4)
N2	0.7889 (1)	0.8210 (2)	0.7831 (2)	0.0223 (4)
N3	0.6380 (1)	0.7262 (2)	0.6973 (2)	0.0183 (3)
N4	0.5723 (1)	0.4265 (2)	0.7359 (2)	0.0233 (4)
N5	0.6390 (1)	0.5902 (2)	0.9359 (2)	0.0240 (4)
N6	0.0440 (1)	0.9560 (2)	1.0223 (2)	0.0188 (3)
N7	0.3610 (1)	0.6590 (2)	0.8222 (2)	0.0195 (4)
C1	0.7099 (1)	0.8608 (3)	0.7121 (2)	0.0166 (4)
C2	0.6173 (1)	0.5769 (3)	0.7933 (3)	0.0178 (4)
H1A	0.742 (2)	1.109 (4)	0.636 (4)	0.056 (9)
H1B	0.638 (2)	1.064 (4)	0.608 (4)	0.036 (7)
H2A	0.830 (2)	0.927 (3)	0.799 (4)	0.036 (7)
H2B	0.806 (1)	0.708 (4)	0.818 (4)	0.038 (8)
H3A	0.596 (1)	0.740 (5)	0.617 (4)	0.031 (6)
H4A	0.545 (2)	0.327 (4)	0.794 (5)	0.041 (7)
H4B	0.576 (2)	0.409 (4)	0.634 (4)	0.045 (8)
H5A	0.645 (2)	0.702 (3)	0.978 (4)	0.031 (6)
H5B	0.629 (2)	0.483 (4)	0.998 (4)	0.032 (7)

Table 3. *Selected geometric parameters ($\mathring{A}$, °) for (BIGH)NO₃ and (BIGH₂)(NO₃)₂*

(BIGH)NO₃		(BIGH₂)(NO₃)₂	
O1—N6	1.253 (1)	O1—N6	1.239 (2)
O2—N6	1.246 (1)	O2—N6	1.241 (2)
O3—N6	1.244 (1)	O3—N6	1.274 (2)
		O4—N7	1.241 (2)
		O5—N7	1.234 (2)
		O6—N7	1.261 (2)
N1—C1	1.320 (2)	N1—C1	1.313 (3)
N2—C1	1.334 (2)	N2—C1	1.307 (2)
N3—C1	1.340 (2)	N3—C1	1.376 (2)
N3—C2	1.334 (2)	N3—C2	1.371 (3)
N4—C2	1.325 (2)	N4—C2	1.317 (3)
N5—C2	1.330 (2)	N5—C2	1.316 (3)
O1—N6—O3	119.5 (1)	O1—N6—O2	120.9 (2)
O2—N6—O3	120.4 (1)	O1—N6—O3	119.1 (2)
O1—N6—O2	120.1 (1)	O2—N6—O3	120.0 (2)
		O4—N7—O5	121.1 (2)
		O4—N7—O6	118.9 (2)
		O5—N7—O6	120.0 (2)
C1—N3—C2	123.4 (1)	C1—N3—C2	126.8 (2)
N1—C1—N2	117.9 (1)	N1—C1—N2	122.5 (2)
N1—C1—N3	116.9 (1)	N1—C1—N3	115.5 (2)
N2—C1—N3	125.0 (1)	N2—C1—N3	121.9 (2)
N3—C2—N4	117.2 (1)	N3—C2—N4	116.5 (2)
N3—C2—N5	125.4 (1)	N3—C2—N5	120.5 (2)
N4—C2—N5	117.4 (1)	N4—C2—N5	123.0 (2)

Table 4. *Hydrogen-bonding geometry ($\mathring{A}$, °) for (BIGH)NO₃ and (BIGH₂)(NO₃)₂*

D—H⋯A	D—H	H⋯A	D—H⋯A
(BIGH)NO₃			
N1—H1A⋯O3ⁱ	0.82 (2)	2.22 (2)	159 (1)
N1—H1B⋯N3ⁱⁱ	0.86 (2)	2.14 (2)	173 (2)
N2—H2A⋯O2ⁱⁱⁱ	0.83 (1)	2.23 (1)	143 (1)
N4—H4B⋯O2ⁱᵛ	0.89 (2)	2.05 (2)	171 (2)
N5—H5A⋯O1ᵛ	0.89 (2)	2.13 (2)	163 (2)
N5—H5B⋯O1ⁱᵛ	0.86 (2)	2.15 (2)	164 (2)

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

$(BIGH_2)(NO_3)_2$

N1—H1A···O6^i	0.86 (3)	2.20 (3)	151 (3)
N1—H1B···O2^{ii}	0.91 (3)	2.05 (3)	154 (3)
N2—H2A···O5^i	0.94 (3)	2.00 (2)	170 (2)
N2—H2B···O4^{iii}	0.87 (3)	2.09 (3)	167 (2)
N3—H3A···O3^{ii}	0.93 (3)	1.83 (3)	168 (3)
N4—H4A···O3^{iii}	0.94 (3)	2.04 (4)	157 (3)
N4—H4B···O4^{iv}	0.92 (4)	2.11 (4)	155 (2)
N5—H5A···O1^i	0.86 (3)	2.20 (2)	150 (3)
N5—H5B···O6^v	0.93 (3)	2.17 (3)	136 (2)

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

Preliminary examinations and intensity data collection were carried out using an Enraf–Nonius CAD-4 diffractometer. Backgrounds were obtained from analysis of the scan profiles (Blessing, Coppens & Becker, 1974). Both structures were solved by direct methods and all atoms, including H atoms, refined cleanly.

For both compounds, data collection: CAD-4 software (Enraf–Nonius, 1977); cell refinement: CAD-4 software; data reduction: *MolEN PROCESS* (Fair, 1990); program(s) used to solve structures: *MULTAN80* (Main *et al.*, 1980); program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *CAChe* (CAChe Scientific, 1993); software used to prepare material for publication: *MolEN CIF IN*.

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5,6,7,8-Tetrahydro-2,3-diphenyl-2aλ⁴-thia-2,3,4a,8a-tetraazacyclopent[cd]azulene-1[2H],4[3H]-diselone

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Abstract

The title compound, $C_{19}H_{18}N_4SSe_2$, crystallizes in the $P\bar{1}$ space group with two molecules in the asymmetric unit. In both molecules, the chemically equivalent halves are identical within experimental error, except for conformational differences which arise from intermolecular interactions between the flexible seven-membered rings and surrounding Se atoms. The central triheterapentalene system is almost planar, with individual ring conformations consistent with three regions of conjugation separated by single bonds. The N—S bond lengths, stretched beyond the standard for a single bond, imply a three-centre interaction.

Comment

We have shown (Billing, Ferg, Lai, Levendis & Reid, 1993) that reaction of the cyclic thioureas [(3); $n = 2, 3, 4, Z = S$] and selenoureas [(3); $n = 2, 3, 4, Z = Se$] with 2,4-dinitrobenzyl chloride followed by deprotonation of the resulting salts with aqueous sodium carbonate yields the bases [(4); $n = 2, 3, 4, Z = S, Se$]. Treatment of the bases [(4); $n = 2, 3, Z = S, Se$] with heterocumulenes RNCX ($X = S, Se$) affords the triheterapentalenes containing the $X—Z—X$ sequence (5) or triheterapentalenes (6) containing the $N—Z—N$ sequence (Lai, 1992), depending on the bridge between the N_a and N_b atoms. To investigate further the influence of the bridge between the N_a and N_b atoms on the