Energetic Materials: The Preparation and Structural Characterization of Three Biguanidinium Dinitramides

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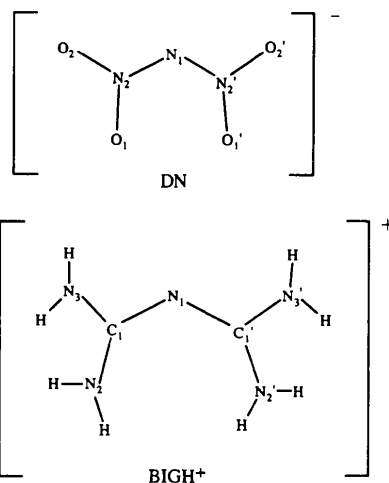
Abstract

Three biguanidinium salts of the energetic dinitramide anion have been prepared and structurally characterized from room-temperature X-ray diffraction data. Biguanidinium mono-dinitramide, (BIGH)(DN), triclinic, $P\bar{1}$, $a = 4.3686\,(4)$, $b = 9.404\,(2)$, $c = 10.742\,(1)$ Å, $\alpha = 83.54\,(1)$, $\beta = 80.386\,(9)$, $\gamma = 79.93\,(1)°$, $V = 426.8\,(1)$ Å^3, $Z = 2$, $D_x = 1.62$ g cm^{-3}. Biguanidinium bis-dinitramide, (BIGH$_2$)(DN)$_2$, monoclinic, $C2/c$, $a = 11.892\,(2)$, $b = 8.131\,(1)$, $c = 13.038\,(2)$ Å, $\beta = 115.79\,(1)°$, $V = 1135.1\,(3)$ Å^3, $Z = 4$, $D_x = 1.84$ g cm^{-3}. Biguanidinium bis-dinitramide monohydrate, (BIGH$_2$)(DN)$_2$.H$_2$O, orthorhombic, $P2_12_12_1$, $a = 6.4201\,(6)$, $b = 13.408\,(1)$, $c = 14.584\,(2)$ Å, $V = 1255.4\,(4)$ Å^3, $Z = 4$, $D_x = 1.76$ g cm^{-3}. All three structures are characterized by extensive hydrogen bonding. Both the mono- and diprotontated cations consist of two planar halves twisted with respect to each other. The dinitramide anion has a surprisingly variable and asymmetric structure. The two halves of the anion are twisted with respect to each other; however, the twist varies from 5.1 to 28.9°. In addition, the two ends of the anion have significantly different geometries, *e.g.* the 'equivalent' N—N bond lengths differ by up to 0.045 Å.
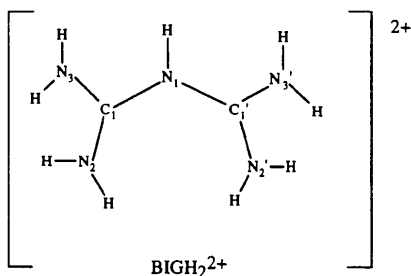
1. Introduction

There is a great deal of current interest in the production of energetic materials (Borman, 1994). A newly discovered class of solid energetic materials is composed of the salts of the dinitramide anion, $N(NO_2)_2^-$, DN, a potent oxidizer. The preparation, characterization and thermal decomposition of the ammonium salt has been described previously (Bottaro, Schmitt, Penwell & Ross, 1991; Schmitt, Krempp & Bierbaum, 1992; Brill, Brush & Patil, 1993; Rossi, Bottaro & McMillen, 1993; Doyle, 1993). More recently, a series of papers has described the preparation and spectral (UV–vis, IR) characterization of the parent acid and a number of other salts (Luk'yanov, Gorelik & Tartakovsky, 1994; Luk'yanov, Konnova, Klimova & Tartakovsky, 1994; Luk'yanov, Anikin, Gorelik & Tartakovsky, 1994; Shlyapochnikov,

Cherskaya, Luk'yanov, Gorelik & Tartakovsky, 1994; Luk'yanov, Shlykova & Tartakovsky, 1994; Luk'yanov, Agevnin, Leichenko Serigina & Tartakovsky, 1995; Shlyapochnikov, Oleneva, Cherskaya, Luk'yanov, Gorelik, Anikin & Tartakovsky, 1995). There have also been reports of theoretical studies of the anion and the parent acid to gain insight into the possible mechanism of decomposition (Michels & Montgomery, 1993; Politzer & Seminario, 1993; Politzer, Seminario, Concha & Redfern, 1993; Mebel, Lin, Morokuma & Melius, 1995). The current paper describes the preparation and structural characterization of three new dinitramide salts, biguanidinium mono-dinitramide, (BIGH)DN (I), biguanidinium bis-dinitramide, (BIGH$_2$)(DN)$_2$ (II), and biguanidinium bis-dinitramide monohydrate, (BIGH$_2$)(DN)$_2$.H$_2$O (III).*†

DN

BIGH+

$BIGH_2^{2+}$

2. Experimental

CAUTION: Dinitramide salts are photosensitive and explosive.

2.1. Preparation of biguanidinium mono-dinitramide, (BIGH)DN

Barium hydroxide (15.7 g, 50 mmol) was suspended in 100 ml of H_2O and ammonium dinitramide [12.5 g, 100 mmol (Bottaro, Schmitt, Penwell & Ross, 1991)] added. The resulting mixture was heated under vacuum in a rotary evaporator until all the ammonia had been removed and the pH was < 8. At this point the aqueous barium dinitramide solution was clear. This was then treated with bis(biguanidinium) sulfate (15 g, 50 mmol) and stirred in the dark for 12 h, followed by filtration. The filtrate was concentrated *in vacuo* and diluted with warm acetonitrile. The resulting solution was passed through a 2.5 × 10 cm silica gel column, eluting with acetonitrile until all the yellow effluent had been collected. This was concentrated to 100 ml and diluted with 200 ml of ethyl acetate. The resulting crystalline precipitate was collected by filtration. Yield 15 g (75%).

2.2. Preparation of biguanidinium bis-dinitramide, (BIGH₂)(DN)₂

Barium dinitramide (100 mmol) in 100 ml of H_2O was prepared as described above and this solution was added to a vigorously stirred suspension of biguanidinium monosulfate (21 g, 100 mmol) in 100 ml of H_2O. The resulting suspension was stirred for 2 h, filtered, concentrated and dissolved in ~500 ml of hot acetonitrile; this solution was immediately passed through a 2.5 × 10 cm column of silica, eluting with acetonitrile until all the yellow effluent was recovered. The acetonitrile effluent was concentrated to 100 ml and biguanidinium bis-dinitramide precipitated as dense prisms, mp 399–402 K. Yield 20 g (65%).

Crystals of (BIGH₂)(DN)₂ and (BIGH)(DN) suitable for X-ray analysis were obtained by slow evaporation of acetonitrile solutions. While attempting to obtain crystals of (BIGH₂)(DN)₂ from presumably wet acetonitrile solution, we obtained X-ray quality crystals of (BIGH₂)(DN)₂.H₂O.

Preliminary examination and intensity data collection for (BIGH)DN (sample I) and (BIGH₂)(DN)₂.H₂O

(sample III) were carried out with an Enraf–Nonius CAD-4 diffractometer and for (BIGH₂)(DN)₂ (sample II) with a Siemens *R*3*m/V* diffractometer. For (I) and (III) backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The crystal of the hydrate (III) decomposed (presumably desolvated) badly during data collection; however, the corrected data was still of sufficient quality to solve the structure. All H atoms for (I) and (II) were found and refined cleanly; however, this was not possible for (III). In this case the H atoms of the cation were fixed in ideal positions for sp^2 nitrogen (N—H 0.95 Å) and those for the water molecule constrained to keep the geometry found from a difference-Fourier map. Computer programs for structures (I) and (III) were taken from *MolEN* (Fair, 1990) and those for (III) were taken from *SHELXTL* (Sheldrick, 1985). The figures were prepared with a CAChe workstation (CAChe, 1993). Scattering factors in all cases were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). A summary of crystal data, data collection, structure solution and refinement is given in Table 1. Final refined parameters and derived geometrical values are reported in Tables 2–10. Drawings of the cations and anions along with the hydrogen-bonding schemes are presented in Figs. 1–3. Semi-empirical molecular orbital calculations (AM1 basis set) were carried out for various geometries of the dinitramide anion with a CAChe workstation (CAChe, 1993).

3. Results and discussion

Compound (I) is composed of one dinitramide anion and one monoprotonated biguanidinium cation in a hydrogen-bonded lattice. Compound (II) contains a diprotonated biguanidinium cation which lies on a crystallographic twofold axis and two dinitramide anions per biguanidinium moiety, again in a hydrogen-bonded network. Compound (III) is composed of two unique dinitramide anions, a diprotonated biguanidinium cation and a water molecule in a lattice which is also characterized by strong hydrogen bonds.

3.1. Biguanidinium cations

The mono- and diprotonated biguanidinium cations in these salts present no surprises. They are composed of two planar halves twisted with respect to each other [with approximate (I, III) or exact (II) twofold symmetry], as has been previously observed for other salts of these cations (Martin, Pinkerton & Schiemann, 1996; Martin & Pinkerton, 1996; Pinkerton & Schwarzenbach, 1978; Ernst, 1977). For (BIGH)⁺ all the bond lengths and angles fall close to values previously observed; however, (I) has the smallest twist yet observed for this cation [34.2 (1)° compared with the literature range 37.8–49.1°]. In the diprotonated cation we again find distances and angles close to known structures, how-

Table 1. *Experimental details*

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_2H_8N_5^+.N_3O_4^-$	$C_2H_9N_5^{2+}.2N_3O_4^-$	$C_2H_9N_5^{2+}.2N_3O_4^-.H_2O$
Chemical formula weight	208.14	315.20	333.18
Cell setting	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P2_12_12_1$
a (Å)	4.3686 (4)	11.892 (2)	6.4201 (6)
b (Å)	9.404 (2)	8.131 (1)	13.408 (1)
c (Å)	10.742 (1)	13.038 (2)	14.584 (2)
α (°)	83.54 (1)		
β (°)	80.386 (9)	115.79 (1)	
γ (°)	79.93 (1)		
V (Å^3)	426.8 (1)	1135.1 (3)	1255.4 (4)
Z	2	4	4
D_x (Mg m^{-3})	1.62	1.844	1.76
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	1.54178	0.71073
No. of reflections for cell parameters	25	25	91
θ range (°)	8–17	39–50	9–14
μ (mm^{-1})	0.14	1.59	0.16
Temperature (K)	294 (1)	293 (2)	294 (1)
Crystal form	Parallelpiped	Clear chunky bipyramids	Tabular
Crystal size (mm)	0.28 × 0.22 × 0.10	0.38 × 0.36 × 0.22	0.33 × 0.24 × 0.24
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Siemens $R3m/V$	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	ψ scans (North, Phillips & Mathews, 1968)	None	ψ scans (North, Phillips & Mathews, 1968)
T_{min}	0.9667	–	0.8915
T_{max}	0.9989	–	0.9784
No. of measured reflections	1917	927	1462
No. of independent reflections	1683	845	1439
No. of observed reflections	1227	812	992
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.025	0.0211	0.030
θ_{max} (°)	25.97	60.05	25.97
Range of h, k, l	$0 \rightarrow h \rightarrow 5$	$0 \rightarrow h \rightarrow 13$	$0 \rightarrow h \rightarrow 7$
	$-11 \rightarrow k \rightarrow 11$	$-9 \rightarrow k \rightarrow 0$	$0 \rightarrow k \rightarrow 16$
	$-13 \rightarrow l \rightarrow 13$	$-14 \rightarrow l \rightarrow 13$	$0 \rightarrow l \rightarrow 17$
No. of standard reflections	3	3	3
Frequency of standard reflections	50 min	Every 100 reflections	50 min
Intensity decay (%)	2.81	0.50	77.31
Refinement			
Refinement on	F	F^2	F
R	0.041	0.0533(F)	0.040
wR	0.038	0.1379	0.032
S	2.231	1.128	2.565
No. of reflections used in refinement	1227	845	992
No. of parameters used	160	115	205
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	H atoms riding
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 0.9237P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$	0.010	<0.001	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.28	0.314	0.41
$\Delta\rho_{min}$ (e Å^{-3})	−0.23	−0.403	−0.24
Extinction method	Isotropic (Zachariasen, 1963)	SHELXL (Sheldrick, 1985)	None
Extinction coefficient	0.12×10^{-4}	0.0343 (27)	
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for X-ray Crystallography (1974, Vol. IV)
Computer programs			
Data collection	CAD-4 (Enraf–Nonius, 1977)	P3/PC (Siemens, 1989a)	CAD-4 (Enraf–Nonius, 1977)
Cell refinement	CAD-4 (Enraf–Nonius, 1977)	P3/PC (Siemens, 1989a)	CAD-4 (Enraf–Nonius, 1977)
Data reduction	PROCESS, MolEN (Fair, 1990), SORTAV (Blessing, 1987)	XDISK (Siemens, 1989b)	PROCESS, MolEN (Fair, 1990), SORTAV (Blessing, 1987)
Structure solution	Direct methods (SIR; Burla et al., 1989)	SHELXS86 (Sheldrick, 1990)	Direct methods (SIR; Burla et al., 1989)
Structure refinement	LSFM MolEN (Fair, 1990)	SHELXL92 (Sheldrick, 1992)	LSFM MolEN (Fair, 1990)
Preparation of material for publication	CIF VAX, MolEN (Fair, 1990)	SHELXTL (Sheldrick, 1985)	CIF VAX, MolEN (Fair, 1990)

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

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

	x	y	z	U_{eq}
O1	0.8727 (5)	0.2858 (2)	0.5605 (2)	0.0756 (6)
O2	1.2289 (4)	0.0993 (2)	0.5560 (2)	0.0581 (5)
O3	0.4431 (4)	0.2823 (2)	0.7474 (2)	0.0531 (5)
O4	0.4503 (4)	0.0766 (2)	0.8587 (1)	0.0518 (5)
N1	0.9784 (4)	0.1661 (2)	0.6033 (2)	0.0392 (5)
N2	0.8413 (4)	0.0882 (2)	0.7083 (2)	0.0379 (5)
N3	0.5687 (4)	0.1571 (2)	0.7706 (2)	0.0365 (5)
N4	1.6236 (6)	−0.4174 (2)	0.6553 (2)	0.0564 (7)
N5	1.4776 (5)	−0.1840 (2)	0.7044 (2)	0.0482 (6)
N6	1.3878 (4)	−0.3812 (2)	0.8562 (2)	0.0369 (5)
N8	1.1499 (5)	−0.3622 (2)	1.0591 (2)	0.0445 (6)
N7	0.9755 (5)	−0.1878 (2)	0.9122 (2)	0.0471 (6)
C1	1.4884 (5)	−0.3244 (2)	0.7405 (2)	0.0361 (6)
C2	1.1737 (5)	−0.3076 (2)	0.9390 (2)	0.0335 (6)
H1	1.612 (6)	−0.510 (3)	0.672 (2)	0.076 (9)
H2	1.719 (6)	−0.388 (3)	0.587 (2)	0.067 (8)
H3	1.408 (5)	−0.117 (3)	0.768 (2)	0.064 (8)
H4	1.544 (5)	−0.159 (2)	0.633 (2)	0.046 (7)
H5	0.834 (5)	−0.145 (2)	0.981 (2)	0.055 (7)
H6	0.972 (5)	−0.153 (2)	0.843 (2)	0.048 (7)
H7	0.993 (5)	−0.331 (2)	1.113 (2)	0.059 (7)
H8	1.293 (5)	−0.442 (2)	1.081 (2)	0.059 (7)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (II)*

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

	x	y	z	U_{eq}
N1	0.1469 (2)	−0.4843 (2)	0.9129 (2)	0.0316 (6)
N2	0.1446 (2)	−0.4146 (2)	1.00920 (15)	0.0302 (6)
O1	0.1625 (2)	−0.4891 (2)	1.09534 (15)	0.0580 (7)
O2	0.1298 (2)	−0.2645 (2)	0.99970 (15)	0.0407 (6)
N3	0.1257 (2)	−0.6478 (2)	0.90013 (15)	0.0287 (6)
O3	0.0901 (2)	−0.7336 (2)	0.9577 (2)	0.0456 (6)
O4	0.1413 (2)	−0.7042 (2)	0.8189 (2)	0.0502 (7)
N4	0	−0.0261 (3)	3/4	0.0339 (8)
H4	0	0.074 (5)	3/4	0.043 (10)
C1	0.0750 (2)	−0.0959 (2)	0.7074 (2)	0.0223 (6)
N5	0.1071 (2)	−0.0021 (2)	0.6427 (2)	0.0298 (6)
H5A	0.073 (3)	0.095 (4)	0.619 (2)	0.042 (7)
H5B	0.165 (3)	−0.036 (3)	0.622 (2)	0.045 (7)
N6	0.1139 (2)	−0.2471 (2)	0.7307 (2)	0.0317 (6)
H6A	0.109 (3)	−0.300 (4)	0.783 (3)	0.045 (8)
H6B	0.153 (3)	−0.285 (4)	0.691 (3)	0.056 (9)

Table 3. *Selected geometric parameters ($\mathring{A}$, °) for (I)*

O1—N1	1.210 (2)	N4—C1	1.330 (3)
O2—N1	1.223 (2)	N5—C1	1.329 (3)
O3—N3	1.226 (2)	N6—C1	1.332 (3)
O4—N3	1.245 (2)	N6—C2	1.334 (3)
N1—N2	1.382 (2)	N8—C2	1.329 (3)
N2—N3	1.359 (2)	N7—C2	1.330 (3)
O1—N1—O2	122.2 (2)	C1—N6—C2	122.9 (2)
O1—N1—N2	126.1 (2)	N4—C1—N5	117.4 (2)
O2—N1—N2	111.7 (2)	N4—C1—N6	116.7 (2)
N1—N2—N3	115.7 (2)	N5—C1—N6	125.8 (2)
O3—N3—O4	121.4 (2)	N6—C2—N8	116.6 (2)
O3—N3—N2	126.9 (2)	N6—C2—N7	126.3 (2)
O4—N3—N2	111.6 (2)	N8—C2—N7	117.1 (2)

Table 6. *Selected geometric parameters ($\mathring{A}$, °) for (II)*

N1—N3	1.350 (3)	N3—O4	1.240 (2)
N1—N2	1.388 (3)	N4—C1	1.363 (2)
N2—O1	1.211 (2)	C1—N6	1.302 (3)
N2—O2	1.231 (2)	C1—N5	1.312 (3)
N3—O3	1.227 (2)		
N3—N1—N2	116.0 (2)	O4—N3—N1	112.3 (2)
O1—N2—O2	123.3 (2)	C1'—N4—C1	130.8 (3)
O1—N2—N1	124.7 (2)	N6—C1—N5	121.8 (2)
O2—N2—N1	111.8 (2)	N6—C1—N4	121.8 (2)
O3—N3—O4	122.2 (2)	N5—C1—N4	116.4 (2)
O3—N3—N1	125.4 (2)		

Symmetry codes: (i) $-x, y, \frac{3}{2} - z$.

Table 4. *Hydrogen-bonding parameters ($\mathring{A}$, °) for (I)*

D—H···A	D—H	H···A	D—H···A
N4—H1···O1^i	0.88 (3)	2.39 (3)	131 (2)
N4—H1···O3^i	0.88 (3)	2.23 (3)	163 (3)
N4—H2···O1^{ii}	0.82 (3)	2.44 (3)	159 (3)
N5—H3···O4^{iii}	0.96 (3)	2.21 (3)	152 (2)
N5—H4···O2^{ii}	0.80 (2)	2.16 (2)	174 (3)
N7—H5···O4^{iv}	0.96 (2)	2.04 (3)	173 (2)
N7—H6···N2	0.78 (2)	2.58 (3)	144 (2)
N8—H7···O3^{iv}	0.86 (3)	2.23 (3)	171 (3)
N8—H8···N6^v	0.92 (3)	2.10 (3)	176 (2)

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

Table 7. *Hydrogen-bonding parameters ($\mathring{A}$, °) for (II)*

D—H···A	D—H	H···A	D—H···A
N4—H4···O4^i	0.81 (4)	2.36 (3)	139.8 (7)
N5—H5A···O2^{ii}	0.88 (3)	2.39 (3)	122 (3)
N5—H5A···O3^{iii}	0.88 (3)	2.24 (3)	153 (3)
N5—H5B···O4^{iv}	0.89 (4)	2.49 (3)	144 (2)
N5—H5B···N1^{iv}	0.89 (4)	2.50 (4)	151 (2)
N6—H6A···N1	0.82 (4)	2.16 (3)	161 (3)
N6—H6B···O1^v	0.88 (4)	2.25 (3)	141 (3)

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

ever, the bond angle at the bridging nitrogen in (II) is the largest observed to date [130.8 (3)° compared with the literature range 122.5–127.1°]. The twist angles of 36.2 (1) and 45.2 (2)° for (II) and (III), respectively, also extend the previous range 43.7–48.4°. The nature of the multiple bonding in these cations has been discussed elsewhere (Pinkerton & Schwarzenbach, 1978).

We note that the monoprotonated biguanidinium cations in structure (I) form hydrogen-bonded dimers

across a center of symmetry (Fig. 1a), a motif previously observed for this cation in the analogous nitrate and perchlorate salts (Martin, Pinkerton & Schiemann, 1996; Martin & Pinkerton, 1996).

3.2. Dinitramide anions

The dinitramide anions are composed of two trigonal nitro groups joined by a common N atom. Their overall shape is similar to that of the cations. Short N—N and N—O bonds are indicative of multiple bonding. Thus, one might expect the dinitramide anions to be as symmetrical as the biguanidinium cations, with twofold symmetry and perhaps a twist to remove steric interference between the 'inner' O atoms (O1, O1′). However, this is far from the case

Table 8. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$) for (III)

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

	x	y	z	U_{eq}
O1	0.7839 (7)	−0.2174 (2)	0.0337 (2)	0.065 (1)
O2	0.8055 (6)	−0.2011 (2)	0.1792 (2)	0.061 (1)
O3	0.9628 (5)	−0.0717 (2)	−0.0450 (2)	0.0434 (9)
O4	0.8943 (5)	0.0680 (2)	0.0206 (2)	0.0410 (9)
O5	0.3361 (5)	−0.0874 (2)	0.1207 (2)	0.053 (1)
O6	0.3511 (6)	0.0380 (2)	0.2144 (2)	0.050 (1)
O7	0.3949 (6)	0.2054 (2)	0.0018 (2)	0.049 (1)
O8	0.2300 (5)	0.1954 (2)	0.1322 (2)	0.0437 (9)
O9	0.4366 (5)	−0.1227 (2)	0.3400 (2)	0.0482 (9)
N1	0.8097 (6)	−0.1663 (2)	0.1017 (2)	0.042 (1)
N2	0.8286 (6)	−0.0637 (2)	0.1011 (2)	0.033 (1)
N3	0.8961 (6)	−0.0240 (2)	0.0208 (2)	0.034 (1)
N4	0.3446 (5)	0.0024 (2)	0.1359 (2)	0.035 (1)
N5	0.3603 (6)	0.0567 (2)	0.0585 (2)	0.034 (1)
N6	0.3258 (6)	0.1587 (2)	0.0679 (2)	0.033 (1)
N7	0.7561 (6)	0.1932 (2)	0.1731 (2)	0.035 (1)
N8	0.7253 (6)	0.2108 (2)	0.3274 (2)	0.039 (1)
N9	0.8456 (6)	0.0614 (2)	0.2645 (2)	0.0283 (9)
N10	0.9236 (5)	−0.0769 (2)	0.3495 (2)	0.035 (1)
N11	1.0474 (6)	0.0742 (2)	0.3968 (2)	0.040 (1)
C1	0.7751 (7)	0.1575 (3)	0.2557 (3)	0.029 (1)
C2	0.9400 (7)	0.0196 (3)	0.3400 (2)	0.028 (1)

Table 9. Selected geometric parameters ($\AA$, °) for (III)

O1—N1	1.216 (5)	N2—N3	1.358 (5)
O2—N1	1.223 (5)	N4—N5	1.347 (5)
O3—N3	1.229 (4)	N5—N6	1.392 (5)
O4—N3	1.234 (4)	N7—C1	1.302 (5)
O5—N4	1.226 (4)	N8—C1	1.306 (5)
O6—N4	1.241 (4)	N9—C1	1.373 (5)
O7—N6	1.232 (5)	N9—C2	1.376 (5)
O8—N6	1.225 (5)	N10—C2	1.306 (5)
N1—N2	1.381 (5)	N11—C2	1.303 (5)
O1—N1—O2	122.4 (4)	O7—N6—O8	125.1 (4)
O1—N1—N2	124.6 (4)	O7—N6—N5	111.4 (4)
O2—N1—N2	112.7 (4)	O8—N6—N5	123.4 (4)
N1—N2—N3	115.0 (4)	C1—N9—C2	127.1 (4)
O3—N3—O4	121.5 (4)	N7—C1—N8	121.1 (4)
O3—N3—N2	125.5 (4)	N7—C1—N9	117.6 (4)
O4—N3—N2	113.0 (4)	N8—C1—N9	121.3 (4)
O5—N4—O6	123.1 (4)	N9—C2—N10	116.9 (4)
O5—N4—N5	112.5 (4)	N9—C2—N11	120.9 (4)
O6—N4—N5	124.3 (4)	N10—C2—N11	122.2 (4)
N4—N5—N6	115.9 (4)		

Table 10. Hydrogen-bonding parameters ($\AA$, °) for (III)

D—H···A	D—H	H···A	D—H···A
N7—H1···O4	0.95*	1.98	175
N7—H2···O9ⁱ	0.95*	1.83	169
N8—H3···O1ⁱⁱ	0.95*	2.19	144
N8—H3···O3ⁱⁱ	0.95*	2.22	128
N8—H4···O5ⁱ	0.95*	2.02	143
N9—H5···N2	0.95*	1.97	172
N10—H6···O7ⁱⁱ	0.95*	2.10	169
N10—H7···O2	0.95*	2.19	156
N11—H8···N5ⁱⁱ	0.95*	2.11	156
N11—H9···O1ⁱⁱⁱ	0.95*	2.41	136
N11—H9···O2ⁱⁱⁱ	0.95*	2.44	159
O9—H10···O4ⁱⁱ	0.93†	2.10	150
O9—H11···O6	0.93†	1.97	166

* Calculated hydrogen positions. † Observed hydrogen positions (but not refined). Symmetry codes: (i) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, -y, z + \frac{1}{2}$; (iii) $2 - x, y + \frac{1}{2}, \frac{1}{2} - z$.

Table 11. Comparison of bond lengths in the dinitramide anion using the atom numbering of the scheme with N1—N2′ defined as the longest N—N bond

	(I)	(II)	(IIIa)	(IIIb)
N1—N2	1.382 (2)	1.388 (3)	1.381 (5)	1.392 (5)
N1—N2′	1.359 (2)	1.350 (3)	1.358 (5)	1.347 (5)
N2—O1	1.210 (2)	1.211 (2)	1.216 (5)	1.225 (5)
N2—O2	1.223 (2)	1.231 (2)	1.223 (5)	1.232 (5)
N2′—O1′	1.226 (2)	1.227 (2)	1.229 (4)	1.241 (4)
N2′—O2′	1.245 (2)	1.240 (2)	1.234 (4)	1.226 (4)

and a wide range of 'equivalent' bond lengths and angles is observed. In these three structures the N—N bond lengths vary from 1.347 (5) to 1.392 (5) Å and the difference in the same molecule from 0.023 to 0.045 Å. The N—O bond lengths vary from 1.210 (2) to 1.245 (2) Å, with the 'inner' N2—O1 bonds being shorter than the 'outer' N2—O2 bonds (Table 11). There is some indication that lengthening of the N—N bond tends to shorten the neighboring N—O bonds, but the evidence is weak. The angle at the bridging nitrogen, however, is fairly constant [115.0 (4)–116.0 (2)°]. The bond angles at the terminal N atoms show a striking asymmetry. The N1—N2—O1 angles are all greater than 120° [123.4 (4)–126.9 (2)], perhaps due to steric interaction between the 'inner' O atoms. However, the O1—N2—O2 angles, although smaller, are also

greater than 120° [121.4 (2)–125.1 (4)°]. In contrast, the N1—N2—O2 angles are all significantly smaller [111.4 (4)–113.0 (4)°]. It is difficult to explain this geometry on the basis of simple steric interactions, especially after consideration of the different amounts of twist observed in these molecules. Defining a pseudotorsion angle O1—N2—N2′—O1′, we observe a value of 5.1° in (I) and the range 24.0–28.9° for the other molecules. Even this wide range underestimates the possibilities for this anion, a twist of 42.7° being observed in the ammonium salt (Gilardi, 1996).

3.3. Hydrogen bonding

In (I) the lattice may be described as planes of ions joined by the twisted ends of a biguanidinium 'dimer' (see above), as shown in Figs. 1(a) and (b). The hydrogen-bonding scheme in (II) forms ribbons in the b direction. The hydrogen-bonded network of (III) is more complicated and completely three-dimensional.

3.4. Compound (I)

The dinitramide anion accepts eight hydrogen bonds from five different biguanidinium cations (Fig. 1b). The two shortest hydrogen bonds are associated with the two 'outer' O atoms [O2···H4 2.16 (2), O4···H5 2.04 (3) Å]. Both these bonds are almost linear [174 (3) and 173 (2)°, respectively]. O4 participates in another hydrogen bond to H3 [O4···H3 2.21(3) Å] and this is clearly bent [N5—H3···O4 152 (2)°]. The two 'inner' O atoms have

four hydrogen bonds involving three H atoms from three different biguanidinium cations associated with them. O1 and O3 are bridged by hydrogen bonds from H1 [O1···H1 2.39 (3), O3···H1 2.23 (3) Å]. Both O1 and O3 accept an additional hydrogen bond [O1···H2 2.44 (3), O3···H7 2.23 Å], as expected, the shorter having the more linear bond [159 (3) versus 171 (3)°]. The longest hydrogen bond [2.58 (3) Å] is formed by the bridging nitrogen with a N7—H6···N2 bond angle of 144 (2)°. Although this is a rather long bond with a small bond angle, its absence would imply no hydrogen bond to the lone pair on the bridging N atom of the anion.

Every hydrogen of the biguanidinium cation is involved in at least one hydrogen bond. The two

hydrogen bonds which hold the dimer together (see above) are symmetry related. The N6···H8 distance is 2.10 (3) Å and the bond is almost linear [N6···H8—N8 176 (2)°].

3.5. Compound (II)

The twofold axis considerably reduces the complexity of the hydrogen bonding (Figs. 2a and b). All the biguanidinium H atoms are hydrogen bonded, with a H···X (X = N, O) contact distance less than 2.5 Å. The H4 atom has a bifurcated bond about the twofold axis [O4···H4 2.36 (4) Å]. H5A is also involved in a bifurcated hydrogen bond, although it is less symmetrical than H4 [O3···H5A 2.24 (3), O2···H5A 2.39 (3) Å]. There are three hydrogen bonds remaining, O1···H6B [2.25 (3)Å], which is
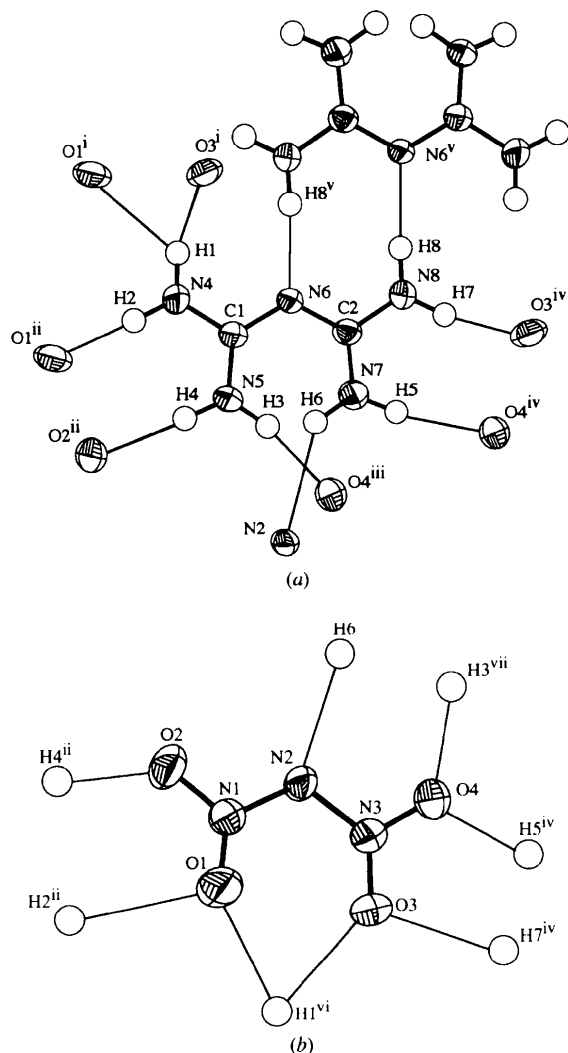

Fig. 1. ORTEP (CAChe, 1993; Johnson, 1965) plots of (a) the monoprotonated biguanidinium cation and (b) the dinitramide anion in (I), showing the atom labeling and hydrogen-bonding scheme; symmetry codes: (i) x + 1, y − 1, z; (ii) 3 − x, −y, 1 − z; (iii) x + 1, y, z; (iv) 1 − x, −y, 2 − z; (v) 3 − x, −y − 1, 2 − z; (vi) x − 1, y + 1, z; (vii) x − 1, y, z.

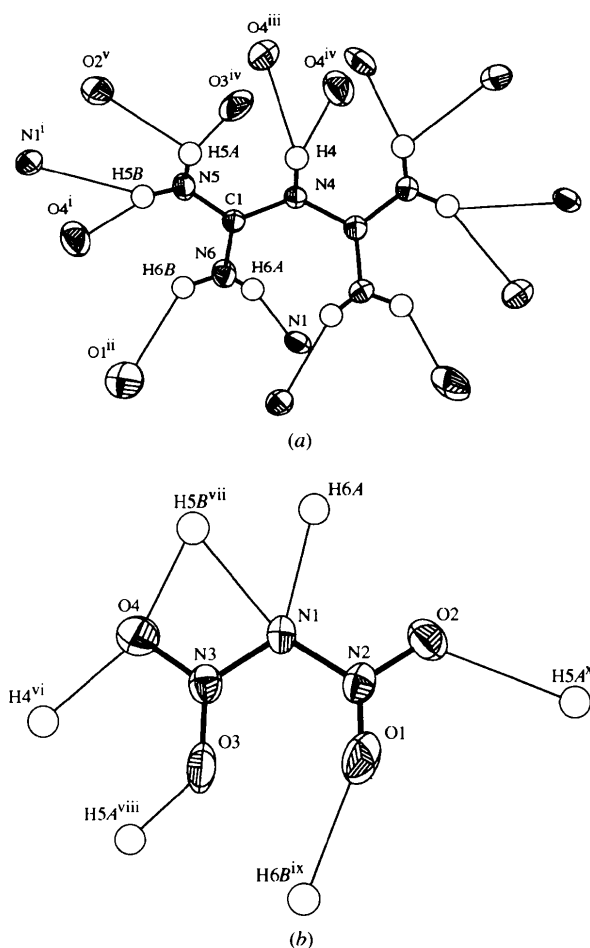Fig. 2. ORTEP (CAChe, 1993; Johnson, 1965) plots of (a) the diprotonated biguanidinium cation and (b) the dinitramide anion in (II), showing the atom labeling and hydrogen-bonding scheme; symmetry codes: (i) ½ − x, y + ½, 3/2 − z; (ii) x, −y − 1, z − ½; (iii) x, y + 1, z; (iv) −x, y + 1, 3/2 − z; (v) x, −y, z − ½; (vi) x, y − 1, z; (vii) ½ − x, y − ½, 3/2 − z; (viii) −x, y − 1, 3/2 − z; (ix) x, −y − 1, z + ½; (x) x, −y, z + ½.

unremarkable, N1···H6A [2.16(3) Å], which is the shortest hydrogen bond in the structure, and the bifurcated bonds of H5B (O4···H5B and N1···H5B), which are the longest [2.50(4) Å]. Looking at the hydrogen bonding to the dinitramide, a pattern quickly emerges, bridging nitrogen < inner oxygen (agrees to within 0.01 Å) < outer oxygen (agrees to within 0.03 Å), each being ~0.1 Å longer than the previous.

3.6. Compound (III)*

In the hydrate there are 13 hydrogen bonds which are all less than 2.5 Å in length. All the H atoms on the biguanidinium cation participate in 11 hydrogen bonds

* Although the H-atom positions were not refined in this structure, reasonable positions can be calculated for the NH_2 groups assuming sp^2 geometry at nitrogen and, although unrefinable, the water hydrogens were observed in the difference-Fourier map. The discussion of the hydrogen bonding is based on these positions.

(Figs. 3a–d), of which four are bifurcated (O1···H3 2.19 and O3···H3 2.22, O1···H9 2.41 and O2···H9 2.44 Å). We note that H3 is bound to the two inner O atoms of a dinitramide anion and that H9 is bound to the inner and outer oxygen of one end of the same dinitramide anion. Two of the short hydrogen bonds and a longer one are also formed with this dinitramide anion in an almost planar 'W' motif; these are O4···H1, N2···H5 and O2···H7 (1.98, 1.97 and 2.19 Å, respectively). It also suggests that the central nitrogen on the dinitramide has a lone pair associated with it. The two short bonds are almost linear (N7—H1···O4 175 and N9—H5···N2 172°), while the longer bond is bent (N10—H7···O2 156°). The second dinitramide anion is less strongly hydrogen bonded, however, the N5···H8 interaction (2.11 Å) again implies a lone pair on the bridging nitrogen.

The water molecule has three hydrogen bonds associated with it. The O9 atom accepts the shortest

Fig. 3. ORTEP (CAChe, 1993; Johnson, 1965) plot of (a) the diprotonated biguanidinium cation, (b) the first dinitramide anion, (c) the second dinitramide anion and (d) the water molecule in (III), showing the atom labeling and hydrogen-bonding scheme; symmetry operations: (i) $\frac{3}{2}$ − x, −y, z + $\frac{1}{2}$; (ii) 1 − x, y + $\frac{1}{2}$, $\frac{1}{2}$ − z; (iii) 2 − x, y + $\frac{1}{2}$, $\frac{1}{2}$ − z; (iv) $\frac{3}{2}$ − x, −y, z − $\frac{1}{2}$; (v) 2 − x, y − $\frac{1}{2}$, $\frac{1}{2}$ − z; (vi) 1 − x, y − $\frac{1}{2}$, $\frac{1}{2}$ − z.

hydrogen bond in the molecule (O9···H2 1.83 Å), which is almost linear (N7—H2···O9 169°). The two water H atoms donate to O atoms on different dinitramide anions (O4···H10 2.10, O6···H11 1.97 Å) and are less linear (O9—H10···O4 150, O9—H11···O6 166°). Thus, the water molecule can be considered as hydrogen bonding 'glue' in this structure, bonding to each of the unique ions.

3.7. Bonding in the dinitramide anion

The dinitramide ion is a relatively new anion and there are no reported crystal structures. As discussed above, it shows some very unusual geometrical variations, in particular, the nonequivalence of the N—N bonds and the variation in the pseudotorsion angle.

Two theoretical descriptions of the central nitrogen have been presented by Politzer, Seminario, Concha & Redfern (1993), depending on whether the anion is twisted or not. If the dinitramide is twisted with an N—N—N angle of 112.4° (their *ab initio* minimum structure, see below), they suggest that the electron pairs are tetrahedrally distributed, thus allowing the NO_2 to twist, separating the inner O atoms and yet remaining conjugated to the central nitrogen. The second interpretation refers to planar dinitramide with the lone pairs in different orbitals on the bridging nitrogen, an sp^2 orbital in the NNN plane and a *p*-orbital perpendicular to it to conjugate to both NO_2 groups.

The experimental N—N—N angles are intermediate between the ideal tetrahedral and trigonal planar geometries. The bridge and pseudotorsion angles appear to be uncorrelated. The ammonium salt (Gilardi, 1996) is an outlier having the smallest bridge angle yet observed (N—N—N, 113.2°). The most reasonable conclusion is that the best description of the bridging nitrogen lies between the two extremes. This has the advantage of delocalizing all the lone pairs on the bridging nitrogen by allowing conjugation with both NO_2 groups. None of these interpretations of the electronic structure of the central nitrogen explain the N—N bond inequivalence.

There have been high-level gas-phase *ab initio* calculations (Michels & Montgomery, 1993) on the dinitramide anion. These calculations used RHF/6-31G** and MP2/6-31G** geometry optimizations to produce a minimum energy structure with C_2 symmetry in both cases. The paper also reported two other structures as transition states, one of which had C_{2v} symmetry. The reported barrier to rotation about the N—N bond was < 1.26 kJ mol^{-1}, which would account for the wide range of observed pseudotorsion angles. Using their minimized geometry we calculate a pseudotorsion angle of 43.0°. Clearly, the twofold symmetry does not allow any difference in the N—N bond lengths.

Michels & Montgomery (1993) point out that rotation of one NO_2 group perpendicular to the other produces a transition state structure that has N—N bond lengths

that differ by ~0.1 Å. If this rotation were responsible for the experimental difference, there should be a strong correlation between the pseudotorsion angle and bond inequivalence; however, there is none. There have also been nonlocal density functional theory calculations carried out on the dinitramide anion (Politzer, Seminario, Concha & Redfern, 1993). This approach, like the *ab initio* calculations, produced a twisted dinitramide group. Using their bond lengths and angles we find a pseudotorsion angle of 40.6°. The N—N bond lengths did not significantly differ in length (1.407, 1.402 Å); however, the inner N—O bond lengths are shorter than the outer ones, in agreement with the crystal structures, and in contrast to the results of Michels & Montgomery (1993).

In order to gain some insight into the possible cause of these variations we have examined the shapes of the frontier orbitals obtained from semi-empirical calculations (AM1). Point calculations were carried out using the geometries of the dinitramide anion obtained from the crystal structures of the mono-protonated biguanidinium and di-protonated biguanidinium salts described above, and also from the crystal structure of the ammonium salt (Gilardi, 1996), which all produced noticeably asymmetric frontier orbitals. A similar point calculation was carried out using the *ab initio* minimum geometry, however, the frontier orbitals now had quite different shapes.

By carrying out additional point calculations, it was found that, in order to produce MO's of similar shape to those found with the experimental geometries, it is necessary that the N—N bonds be inequivalent and that there be some twist (an asymmetric planar geometry was also tested). The orbital shapes are also sensitive to the N—N—N angle. We conclude that symmetry breaking is important and that, because reducing the symmetry from C_{2v} to C_2 did not produce much change in the orbitals, A/B orbital mixing must be important. The result of the symmetry breaking is that there are two different frontier orbitals with significant contributions along the N—N bonds.

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