organic papers

N,N-Dimethylbiguanidium bromide

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The crystal structure of the title compound, $C_4H_{12}N_5^+ \cdot Br^-$, shows that the C—N bonds in this compound range in length from 1.316 (4) to 1.354 (4) Å. The dihedral angle between the two guanide planes is 68.5 (1)°. The crystal packing is stabilized by N—H$\cdots$N and N—H$\cdots$Br hydrogen bonds. The bromide anions are involved in six hydrogen bonds and are sandwiched between layers of N,N-dimethylbiguanidium cations.

Comment

An N-substituted derivative of biguanide, N,N-dimethylbiguanide, is a powerful oral antihyperglycaemic drug that has been used in many countries for over 40 years for treating diabetic patients with non-insulin-dependent diabetes mellitus. The crystal structures of N,N-dimethylbiguanide reacted with different acids, such as hydrochloric and nitric acid, have been studied (Hariharan et al., 1989; Zhu et al., 2003). We report here the crystal structure of N,N-dimethylbiguanidium bromide, (I).

(I)
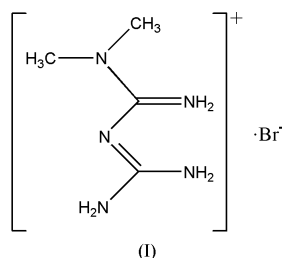
The molecular conformation of (I) is illustrated in Fig. 1. The C—N bonds range in length from 1.316 (4) to 1.354 (4) Å, similar to those observed in related structures (Hariharan et al., 1989; Zhu et al., 2003), and indicating delocalization of electron density. The dihedral angle between the two guanide planes is 68.5 (1)°, which is comparable with that in N,N-dimethylbiguanidium hydrochloride, but larger than that [51.7 (1)°] in N,N-dimethylbiguanidium nitrate. This difference results from the fact that, in N,N-dimethylbiguanidium nitrate, a pair of cations are linked to each other by hydrogen
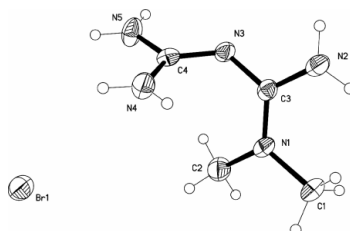

Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 40% probability level.

bonds through atoms N3 and N5; however, *N,N*-dimethyl-biguanidium hydrochloride and bromide do not involve such interactions and, therefore, have more freedom between the two guanide groups.

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Fig. 2. The molecules in the crystal structure are stabilized by N—H···N and N—H···Br hydrogen bonds. The bromide anions are involved in six hydrogen bonds and are sandwiched between layers of *N,N*-dimethylbiguanidium cations.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China without further purification. *N,N*-Dimethylbiguanide was obtained from a 1:1 molar ratio of *N,N*-dimethylbiguanidium hydrochloride and NaOH in 2-propanol. The suspension was stirred for 1 h at 313 K, filtered, and the filtrate evaporated to yield a white solid free of Cl^- (checked with 0.1 *M* $AgNO_3$ solution). Compound (I) was prepared by dissolving *N,N*-dimethylbiguanide (10.0 mmol) in 5 ml water with the addition of hydrogen bromide to adjust the pH to 4. The solution was left at room temperature and crystals of the compound appeared from the solution after several weeks, by slow evaporation of the solvent.

Crystal data

$C_4H_{12}N_5^+ \cdot Br^-$	$D_x = 1.623$ Mg m^{-3}
$M_r = 210.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2039
$a = 8.2094 (18)$ Å	reflections
$b = 14.203 (3)$ Å	$\theta = 2.7$–$26.8°$
$c = 8.1261 (18)$ Å	$\mu = 4.72$ mm^{-1}
$\beta = 114.807 (3)°$	$T = 298 (2)$ K
$V = 860.1 (3)$ Å^3	Block, white
$Z = 4$	$0.70 \times 0.50 \times 0.50$ mm

Data collection

|	
Bruker SMART 1K CCD area-detector diffractometer	1516 independent reflections
	1237 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.069$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)	$\theta_{max} = 25.0°$
$T_{min} = 0.064$, $T_{max} = 0.094$	$h = -9 \rightarrow 7$
4122 measured reflections	$k = -16 \rightarrow 16$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$
$wR(F^2) = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$
1516 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
93 parameters	$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C3—N2	1.324 (4)	C4—N3	1.316 (4)
C3—N1	1.324 (4)	C4—N5	1.330 (4)
C3—N3	1.354 (4)	C4—N4	1.331 (4)
N2—C3—N1	120.5 (3)	N3—C4—N4	124.3 (3)
N2—C3—N3	116.8 (3)	N5—C4—N4	117.2 (3)
N1—C3—N3	122.4 (3)	C4—N3—C3	122.6 (2)
N3—C4—N5	118.4 (3)		
N1—C3—N3—C4	58.1 (4)		
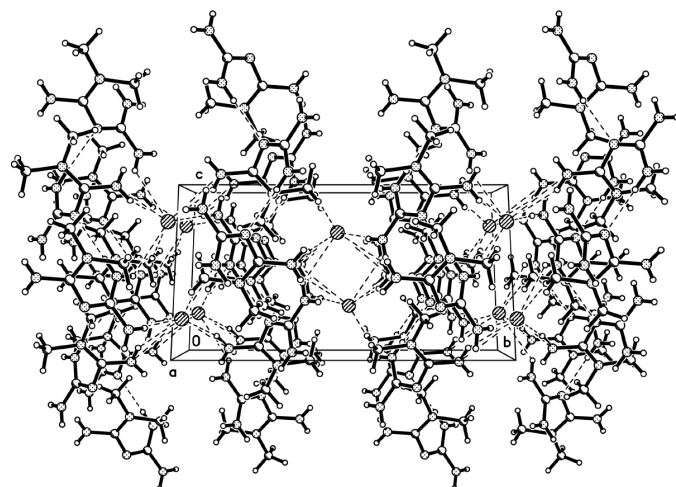
Figure 2
A packing diagram of the structure of the title compound. Hydrogen bonds are indicated by dashed lines.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5B···Br1^i	0.86	2.55	3.400 (3)	169
N5—H5A···Br1^{ii}	0.86	2.77	3.460 (3)	139
N4—H4B···Br1^i	0.86	3.14	3.867 (3)	144
N4—H4B···Br1	0.86	2.87	3.469 (3)	128
N4—H4A···N3^{iii}	0.86	2.18	3.017 (4)	165
N2—H2E···Br1^{iv}	0.86	2.64	3.422 (3)	152
N2—H2D···Br1^v	0.86	2.62	3.422 (3)	155

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

H atoms attached to C and N atoms were placed in geometrically idealized positions, with Csp^3—H = 0.96 Å and Nsp^2—H = 0.86 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(N)$, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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