

Nitroguanyl azide

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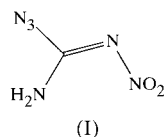
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Crystals of the title compound, nitrocarbamidoyl azide, $\text{CH}_2\text{N}_6\text{O}_2$, consist of two symmetry-independent molecules and the structure is stabilized by intra- and intermolecular hydrogen bonds. The molecule possesses a nitrimine structure.

Comment

Nitroguanyl azide, or 1-azido-*N*-nitroformidine, (I), is an interesting high energy compound (Lieber *et al.*, 1951). The question of whether (I) is a primary nitramine or a nitrimine still remains open. In earlier work, (I) was considered to be a primary nitramine (Lieber *et al.*, 1951; Henry & Boschan, 1954; Henry *et al.*, 1955; Scott *et al.*, 1956). As the reaction ability, in particular the thermal stability, varies greatly for nitrimines and primary nitramines (Astachov, 1999), the question of the molecular structure of (I) is key to understanding its thermal decomposition mechanism. In addition, if (I) is a primary nitramine, there is a complication in the definition of the reaction centre of thermal decomposition, since azide and primary nitramine groups are rather similar in thermal stability. In order to elucidate the structure of (I), an X-ray crystal structure analysis has been undertaken and the results are presented here.



The structure of (I) consists of four molecules in a triclinic unit cell. Each of the two symmetry-independent molecules, *A* and *B*, has a planar conformation (Fig. 1), stabilized by an $\text{N2}-\text{H2}\cdots\text{O2}$ intramolecular hydrogen bond and enhanced by favourable π -orbital overlap. Deviations from the least-squares plane through the non-H atoms are 0.026 (1) (r.m.s.) and 0.055 (1) Å (maximum) for molecule *A*, and 0.046 (1) (r.m.s.) and 0.061 (1) Å (maximum) for molecule *B*.

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The geometric parameters of the intramolecular hydrogen bonds (Table 2) are nearly equal to those of other nitroguanidine derivatives (Choi, 1981; Nordenson, 1981*a,b*; Nordenson & Hvoslef, 1981; Oyumi *et al.*, 1987; Gao *et al.*, 1991). The intermolecular $\text{N2A}-\text{H1A}\cdots\text{O1B}$ and $\text{N2B}-\text{H1B}\cdots\text{O1A}$ hydrogen bonds form a one-dimensional molecular chain of the *A-B-A-B* type. Two adjacent chains are connected by an intermolecular $\text{N2B}-\text{H2B}\cdots\text{O2B}'$ hydrogen bond (Table 2) to form ribbons along the cell *b* axis (Fig. 2). It is worth noting that the $\text{N2B}-\text{H2B}$ group is involved in both inter- and intramolecular hydrogen bonding at the same time.

We conclude that, in the solid state, (I) is not a primary nitramine, as was considered earlier, but possesses a nitrimine structure. Similar to other nitrimines (Choi, 1981; Nordenson, 1981*a,b*; Nordenson & Hvoslef, 1981; Oyumi *et al.*, 1987; Gao *et al.*, 1991), the values of the N–N and C–N bond lengths (Table 1) in the nitrimine fragment of the molecule of (I) are intermediate between the values characteristic of single and double bonds. This indicates a delocalization of the electron density of the nitrimine fragment of the molecule, resulting in a decrease of the N–NO₂ bond distance, a lengthening of the N–O bonds and an averaging of the C–N bonds. The determination of a nitrimine structure for (I) allows us to consider unequivocally that the azide function is the reaction centre which is responsible for thermal decomposition of the compound. The C–N₃ bond length [1.392 (2) and 1.389 (2) Å in molecules *A* and *B*, respectively] is much shorter than in aliphatic azides (1.47 Å for CH_3-N_3) and indicates the

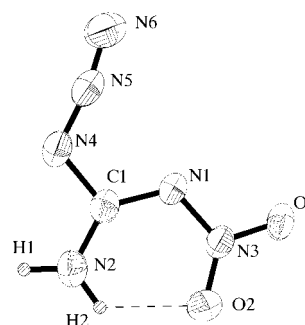


Figure 1

Molecule *A* of (I) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

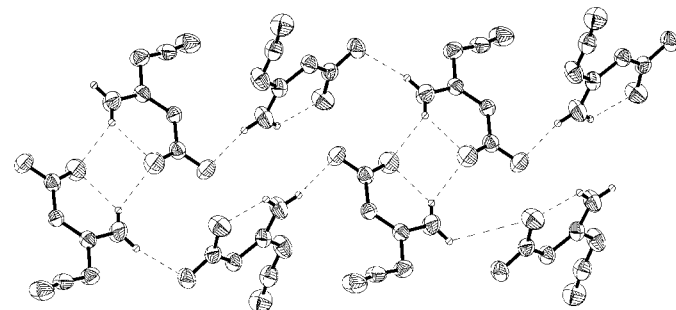


Figure 2

The hydrogen-bonding scheme in (I).

conjugation of the azide group with the delocalized π -electron density of the nitrime fragment of the molecule. The presence of such a conjugation promotes the thermal decomposition of the azide function (Manelis *et al.*, 1996) and, consequently, the thermal stability of (I) is expected to be lower in comparison with aliphatic and even aromatic azides, and this is observed in practice (Astachov, 2000).

Experimental

Caution: the title compound should be treated as a dangerous explosive! Compound (I) was synthesized as described earlier by Lieber *et al.* (1951). Single crystals were obtained by evaporation in air of an aqueous solution of (I), which was acidified with HCl to pH < 1 (in a neutral aqueous environment, (I) is isomerized to 5-nitraminotetrazole).

Crystal data

CH ₂ N ₆ O ₂	Z = 4
M _r = 130.09	D _x = 1.701 Mg m ⁻³
Triclinic, P1̄	Cu K α radiation
a = 9.9302 (8) Å	Cell parameters from 24 reflections
b = 7.9433 (9) Å	θ = 26–34°
c = 7.1288 (8) Å	μ = 1.37 mm ⁻¹
α = 98.310 (10)°	T = 293 (2) K
β = 110.580 (10)°	Lump, colourless
γ = 75.108 (9)°	0.32 × 0.30 × 0.29 mm
V = 507.83 (9) Å ³	

Data collection

Kuma KM-4 four-circle diffractometer	θ_{\max} = 70°
Profile measured $\theta/2\theta$ scans	h = -12 → 0
1971 measured reflections	k = -9 → 9
1851 independent reflections	l = -8 → 8
1713 reflections with $I > 2\sigma(I)$	2 standard reflections every 50 reflections
R _{int} = 0.015	intensity decay: none

Refinement

Refinement on F ²	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.1095P]$
R(F) = 0.034	where $P = (F_o^2 + 2F_c^2)/3$
wR(F ²) = 0.095	(Δ/σ) _{max} = 0.009
S = 1.09	$\Delta\rho_{\max}$ = 0.21 e Å ⁻³
1851 reflections	$\Delta\rho_{\min}$ = -0.20 e Å ⁻³
180 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
All H-atom parameters refined	Extinction coefficient: 0.0089 (14)

Table 1

Selected geometric parameters (Å).

C1A–N1A	1.3296 (18)	C1B–N1B	1.3343 (17)
C1A–N2A	1.303 (2)	C1B–N2B	1.3024 (18)
C1A–N4A	1.3921 (18)	C1B–N4B	1.3891 (18)
N1A–N3A	1.3532 (15)	N1B–N3B	1.3531 (16)
N4A–N5A	1.257 (2)	N4B–N5B	1.2566 (17)
N5A–N6A	1.1104 (19)	N5B–N6B	1.1104 (18)

Table 2

Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N2A–H2A...O2A	0.88 (3)	1.99 (2)	2.608 (2)	126 (2)
N2B–H2B...O2B	0.86 (2)	2.01 (2)	2.589 (2)	123 (2)
N2A–H1A...O1B ⁱ	0.89 (3)	2.21 (3)	3.088 (2)	167 (2)
N2B–H1B...O1A ⁱⁱ	0.83 (3)	2.07 (3)	2.880 (2)	164 (2)
N2B–H2B...O2B ⁱⁱⁱ	0.86 (2)	2.29 (2)	3.056 (2)	148 (2)

Symmetry codes: (i) 1 - x, -y, 1 - z; (ii) 1 - x, 1 - y, -z; (iii) -x, 1 - y, -1 - z.

Data collection: *KM-4 Software* (Kuma, 1991); cell refinement: *KM-4 Software*; data reduction: *DATARED* in *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1067). Services for accessing these data are described at the back of the journal.

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