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1,2-Dinitroguanidine

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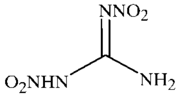
The title compound, $CH_3N_5O_4$, is almost planar, and the conformation is fixed by two intramolecular N—H···O hydrogen bonds. Owing to the delocalization of π-electron density over the whole molecule, there is through-conjugation, with the C—N, N—N and N—O bond lengths having values intermediate between those typical for the corresponding single and double bonds.

Comment

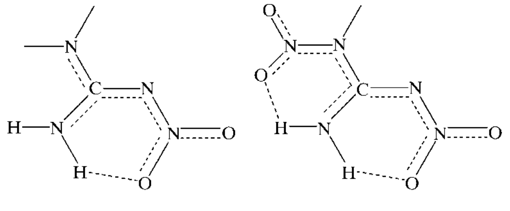
The search for new explosives with more effective physico-chemical properties than those of currently known compounds is one of the more urgent tasks of modern chemical science in most industrially developed countries (Agrawal, 1998; Pagoria *et al.*, 2002). Recently, the synthesis of 1,2-dinitroguanidine, (I), was reported (Astratiev *et al.*, 2003). The compound is of practical interest as an explosive as it has a positive oxygen balance, and it is able to produce salts which will also be explosives. From a chemical standpoint, the compound is interesting because it contains primary nitramine and nitroguanyl groups in the molecule simultaneously. In the present communication, the crystal structure and molecular conformation of (I) are considered.



(I)

A general view of the geometry of (I) is shown in Fig. 1. The molecular guanidine frame is practically planar; deviations from the least-squares plane through atoms C, N2, N3 and N4 are 0.003 (1) (r.m.s.) and 0.005 (1) Å (maximum for the C atom). However, the nitro-group planes are rotated by small angles in opposite directions with respect to the plane of the guanidine fragment [7.9 (3)° for the nitro group of the nitrimine moiety and −7.3 (4)° for the nitro group of the nitramine fragment]. This leads to deviations from the common least-squares plane through all the non-H atoms [r.m.s. deviation = 0.073 (1) Å; maximum deviation = 0.127 (1) Å for atoms O1 and O3].

As in other nitrimines (Allen, 2002), the C—N, N—N and N—O bond lengths in (I) have values intermediate between those typical for the corresponding single and double bonds (Table 1). The formal C—N3 single bond [1.303 (2) Å], not the formal C═N2 double bond [1.341 (2) Å], has the shortest C—N bond distance in the molecule. This peculiarity of the structure, which is associated with the possibility of conjugation and redistribution of the electron density and which contradicts the representation shown in the *Scheme* above, has been observed in other nitrimines (Nordenson, 1981*a*,*b*; Bracuti, 1999; Astachov *et al.*, 2002, 2003; Vasiliev *et al.*, 2003, 2004). The planar configuration of atom N4 (sum of valence angles = 359.5°), the almost planar geometry of the whole molecule and the average bond-length values testify to through-conjugation in the molecule of (I), *i.e.* the propagation of nitrimine-specific delocalization of π-electron density on to the second nitro group [see *Scheme* below, showing (*a*) the delocalization of π-electron density in the nitroguanyl fragment of nitroguanidine and its alkyl derivatives, and (*b*) the 1,2-dinitroguanyl fragment of 1,2-dinitroguanidine or 1-methyl-1,2-dinitroguanidine]. In this regard, the structure of (I) does not differ from the structures of recently reported substituted 1,2-dinitroguanidines (Astachov *et al.*, 2002; Vasiliev *et al.*, 2004).



(*a*) (*b*)

The nitro group, as a strong electron-acceptor substituent, reduces the electron density on atom N4. The possibility of the participation of this atom in the nitrimine conjugation is reduced and, as a consequence, the C—N4 bond length [1.380 (2) Å] increases in comparison with the analogous bond length in a nitroguanidine [1.322 (2) Å; Bracuti, 1999]. The same situation is found in other nitrimines with electron-acceptor substituents, *viz*. 1-methyl-1-nitroso-2-nitroguanidine (Nordenson & Hvoslef, 1981; Rice *et al.*, 1984), nitroguanylazide (Vasiliev *et al.*, 2001), and 1-methyl-1,2-dinitroguanidine and 1-nitro-2-nitriminoimidazolidine (Astachov *et al.*, 2003; Vasiliev *et al.*, 2004), where the lengths of the analogous C—N bond are in the range 1.379–1.408 Å. Nevertheless, the C—N4 bond in (I) is distinctly shorter in comparison with the analogous C—$NHNO_2$ bond in primary alkylnitramines, *viz*. 1.463 (4) Å in 1,2-ethylenedinitramine (Turley, 1968), 1.461 (3) Å in 1,3,5-trinitrazapentane (Zhang *et al.*, 1984) or 1.433–1.443 Å in 1,3-bis(2-nitraminoethyl)urea (Vasiliev *et al.*, 2002). This fact appreciably affects the reaction ability of (I) and, primarily, its thermal stability. It is known

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that thermal decomposition of primary nitramines in the condensed state proceeds along the path of the ionic autoprolitic mechanism, with initial breakage of the C—N bond (Pavlov *et al.*, 1989; Stepanov *et al.*, 1998, 1999; Astachov, 1999). The stronger an acid is the primary nitramine, the less is its thermal stability (Astachov *et al.*, 2000). Compound (I) is a strong acid, with a pK_a value of 1.1 (Astratiev *et al.*, 2003). In spite of this, because of the presence of conjugation between the primary nitramine and nitroguanyl groups, the C—$NHNO_2$ bond in (I) is stronger than in primary alkylnitramines and, consequently, the thermal stability is also higher. However, on the whole, the thermal stability of (I) is not high. The compound flash-decomposes in the solid phase without melting, at 428–438 K, depending on the heating rate. Thus, compound (I) is inferior to secondary nitramines in terms of thermal stability. This is an important characteristic in practice, for example, in the established explosive RDX.

Even in the presence of conjugation between the primary nitramine and the nitroguanyl groups, which strengthens the C—N4 bond, this bond is the weakest C—N bond observed (Table 1). In accordance with this fact, compound (I) and other nitrimines with electron-acceptor substituents (1-methyl-1-nitroso-2-nitroguanidine, 1-methyl-1,2-dinitroguanidine, nitroguanylazide and 1-nitro-2-nitriminoimidazolidine) readily take part in nucleophilic replacement reactions, which are accompanied by the breaking of the C—N4 bond (Astratiev *et al.*, 2003; Astachov *et al.*, 2003; Vasiliev *et al.*, 2004). Nitrimines which do not contain electron-acceptor substituents have an analogous C—N bond length not greater than 1.330 Å (Allen, 2002) and, consequently, an essentially diminished reaction ability in nucleophilic replacement reactions (McKay, 1951).

The molecule of (I) has two intramolecular hydrogen bonds, N3—H1···O1 and N3—H2···O3 (Fig. 1), which result in a flat molecular conformation. The geometrical parameters of these bonds (Table 2) are close to those in other nitrimines (Allen, 2002). The crystal structure contains an intermolecular N4—H3···O2 hydrogen bond between the H atom of the primary nitramine group and an O atom of the nitro group of the nitrimine part of a neighbouring molecule. In addition, there is a possible weak N3—H2···O4′ hydrogen bond between the H atom which participates in the intramolecular hydrogen bond and an O atom of the nitramine group of another molecule. This bond length (Table 2) has an extreme value and even exceeds some geometrical criteria of hydrogen-bond limits (Zefirov & Zorky, 1989). Nevertheless, taking into account that the question of the definition of hydrogen-bond limits is debatable (Steiner, 2000), we consider that the presence of the bond is possible. This is supported by the observation that the N3—H2 bond is longer than the other N—H bonds in the molecule, which may be supposed to be due to the participation of atom H2 in two hydrogen bonds simultaneously. As a result, the O3···O4′ interatomic contact is short [2.749 (2) Å]. Thus, all O and N atoms available in the molecule take part in the formation of hydrogen bonds which connect individual molecules into an infinite structure in the crystal. On the other hand, we cannot confidently affirm that there is an intermolecular N3—H1···O1′ hydrogen bond, because of poor geometry parameters (Table 2). At the same time, there are no N—H···N2 hydrogen bonds in the crystal structure of (I), although these are present in nitroguanidine (Bryden *et al.*, 1956; Choi, 1981; Bracuti, 1999) and some of its derivatives (Nordenson & Hvoslef, 1981; Nordenson, 1981*a*,*b*; Rice *et al.*, 1984; Astachov *et al.*, 2003; Vasiliev *et al.*, 2003). In general, the net of hydrogen bonds in the crystal stucture of (I) is less developed than in nitroguanidine compounds. As a consequence, compound (I) has a less compact molecular packing in the crystal. The calculated value of the molecular packing coefficient ($K_{\rm pack}$) for (I) is 0.693 (Kuzmina *et al.*, 1990; Kuzmin & Katser, 1992). In comparison, $K_{\rm pack}$ = 0.727 for nitroguanidine, $K_{\rm pack}$ = 0.681 for 1-methyl-2-nitroguanidine, and $K_{\rm pack}$ = 0.655 for 1-methyl-1,2-dinitroguanidine, which has no intermolecular hydrogen bonds (Vasiliev *et al.*, 2004).

The density of (I), 1.884 Mg m^{-3}, is high enough, but is less than the density of most known powerful explosives, which have densities in the range 1.9–2.07 Mg m^{-3} (Agrawal, 1998; Pagoria *et al.*, 2002). This does not allow (I) to compete with the latter on energetic parameters.

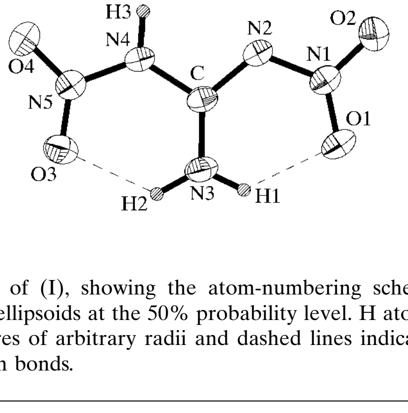

Figure 1

The molecule of (I), showing the atom-numbering scheme and with displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii and dashed lines indicate intramolecular hydrogen bonds.

Experimental

Compound (I) was synthesized as described previously by Astratiev *et al.* (2003). Single crystals were obtained by crystallization of (I) from ethyl acetate.

Crystal data

$CH_3N_5O_4$
M_r = 149.08
Orthorhombic, $P2_12_12_1$
a = 9.6465 (6) Å
b = 10.7694 (7) Å
c = 5.0583 (3) Å
V = 525.49 (6) Å^3
Z = 4
D_x = 1.884 Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 22–25°
μ = 1.65 mm^{-1}
T = 293 (2) K
Block, colourless
0.38 × 0.36 × 0.34 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
702 measured reflections
702 independent reflections
672 reflections with $I > 2\sigma(I)$
$\theta_{\rm max}$ = 79.9°
$h = 0 \rightarrow 12$

$k = 0 \rightarrow 13$
$l = 0 \rightarrow 6$
2 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.066$
$S = 1.00$
702 reflections
103 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.0728P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (2)

Table 1
Selected geometric parameters (Å, °).

N1—O1	1.2312 (18)	C—N4	1.380 (2)
N1—O2	1.2391 (19)	N3—H1	0.88 (3)
N1—N2	1.351 (2)	N4—N5	1.372 (2)
N2—C	1.341 (2)	N5—O4	1.2098 (19)
C—N3	1.303 (2)	N5—O3	1.2142 (18)
O1—N1—O2	121.64 (14)	N2—C—N4	107.52 (13)
O1—N1—N2	124.11 (15)	N5—N4—C	126.55 (13)
O2—N1—N2	114.24 (13)	O4—N5—O3	126.27 (15)
C—N2—N1	118.10 (12)	O4—N5—N4	114.14 (14)
N3—C—N2	130.57 (14)	O3—N5—N4	119.59 (14)
N3—C—N4	121.90 (15)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···O1	0.88 (3)	1.97 (2)	2.601 (2)	128 (1)
N3—H1···O1$^{\rm i}$	0.88 (3)	2.38 (2)	2.917 (2)	120 (1)
N3—H2···O3	0.94 (2)	1.98 (2)	2.648 (2)	126 (1)
N3—H2···O4$^{\rm ii}$	0.94 (2)	2.35 (2)	3.228 (2)	154 (1)
N4—H3···O2$^{\rm iii}$	0.89 (2)	2.03 (2)	2.915 (2)	171 (1)

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

Because the $K\alpha_1$ and $K\alpha_2$ maxima are resolved for the cell-measurement reflections, we used the $K\alpha_1$ maximum for exact determination of the unit-cell parameters. H atoms were found in a difference Fourier map and refined in an isotropic approximation. We did not attempt to define the absolute structure because of the absence of strong anomalous scatterers in the compound.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1658). A packing diagram is also available. Services for accessing these data are described at the back of the journal.

References

Agrawal, J. P. (1998). *Prog. Energy Combust. Sci.* **24**, 1–30.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Astachov, A. M. (1999). PhD thesis, Siberian State Technological University, Krasnoyarsk, Russia.

Astachov, A. M., Stepanov, R. S., Kruglyakova, L. A. & Kekin, Yu. V. (2000). *Energetic Materials – Analysis, Diagnostics and Testing*. 31st International ICT Conference, June 27–30, 2000, Karlsruhe, Germany, pp. 13/1–13/10.

Astachov, A. M., Vasiliev, A. D., Molokeev, M. S., Kekin, Yu. V., Kruglyakova, L. A. & Stepanov, R. S. (2003). *J. Struct. Chem.* **44**, 364–368. (In Russian.)

Astachov, A. M., Vasiliev, A. D., Molokeev, M. S., Kruglyakova, L. A. & Stepanov, R. S. (2002). *New Trends in Research of Energetic Materials*. Proceedings of the Vth Seminar, April 24–25, 2002, Pardubice, Czech Republic, pp. 28–40.

Astratiev, A. A., Dashko, D. V. & Kuznetsov, L. L. (2003). *Zh. Org. Khim.* (*Russ. J. Org. Chem.*), **39**, 537–548. (In Russian.)

Bracuti, A. J. (1999). *J. Chem. Crystallogr.* **29**, 671–676.

Bryden, J. H., Burkardt, L. A., Hughes, E. W. & Donohue, J. (1956). *Acta Cryst.* **9**, 573–578.

Choi, C. S. (1981). *Acta Cryst.* B**37**, 1955–1957.

Kuma (1991). *KM*-4 *Software*. Version 5.2. Kuma Diffraction, Wrocław, Poland.

Kuzmin, V. S. & Katser, S. B. (1992). *Izv. Akad. Nauk Ser. Khim.* (*Russ. Chem. Bull.*), pp. 922–931. (In Russian.)

Kuzmina, N. E., Kuzmin, V. S. & Burtsev, Yu. N. (1990). *Izv. Akad. Nauk Ser. Khim.* (*Russ. Chem. Bull.*), pp. 2866–2869. (In Russian.)

McKay, A. F. (1951). *Chem. Rev.* **51**, 301–346.

Nordenson, S. (1981*a*). *Acta Cryst.* B**37**, 1543–1547.

Nordenson, S. (1981*b*). *Acta Cryst.* B**37**, 1774–1776.

Nordenson, S. & Hvoslef, J. (1981). *Acta Cryst.* B**37**, 373–378.

Pagoria, P. F., Lee, G. S., Mitchell, A. R. & Schmidt, R. D. (2002). *Thermochim. Acta*, **384**, 187–204.

Pavlov, A. N., Fedotov, A. A., Pavlova, L. L., Gamera, Yu. V. & Dubovitskii, F. I. (1989). Proceedings of the 9th Symposium on Combustion and Explosives, November 19–24, 1989, Suzdal-Chernogolovka, USSR, pp. 103–107.

Rice, S., Cheng, M. Y., Cramer, R. E., Mandel, M., Mower, H. F. & Seff, K. (1984). *J. Am. Chem. Soc.* **106**, 239–243.

Sheldrick, G. M. (1995). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stepanov, R. S., Astachov, A. M., Kruglyakova, L. A. & Kekin, Yu. V. (1998). *Energetic Materials – Production, Processing and Characterization*. 29th International ICT Conference, June 30–July 3, 1998, Karlsruhe, Germany, pp. 128/1–129/7.

Stepanov, R. S., Astachov, A. M., Kruglyakova, L. A. & Stepanova, M. A. (1999). *Zh. Obshch. Khim.* (*Russ. J. Gen. Chem.*), **69**, 1695–1698. (In Russian.)

Steiner, T. (2000). *IUCr Newslett.* **8**, 19–20.

Turley, J. W. (1968). *Acta Cryst.* B**24**, 942–946.

Vasiliev, A. D., Astachov, A. M., Kruglyakova, L. A. & Stepanov, R. S. (2002). *J. Struct. Chem.* **43**, 886–889.

Vasiliev, A. D., Astachov, A. M., Molokeev, M. S., Kruglyakova, L. A. & Stepanov, R. S. (2003). *Acta Cryst.* E**59**, o193–o194.

Vasiliev, A. D., Astachov, A. M., Molokeev, M. S., Kruglyakova, L. A. & Stepanov, R. S. (2004). *J. Struct. Chem.* **45**. In the press.

Vasiliev, A. D., Astachov, A. M., Nefedov, A. A., Kruglyakova, L. A. & Stepanov, R. S. (2001). *Acta Cryst.* C**57**, 625–626.

Zefirov, Yu. V. & Zorky, P. M. (1989). *Usp. Khim.* (*Russ. Chem. Rev.*), **58**, 713–746. (In Russian.)

Zhang, H., Yun, G., Xu, C., Ma, Z. & Peng, Z. (1984). *Acta Armamentarii*, pp. 43–48.