Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,6-Diamino-3,5-dinitro-1,4-pyrazine 1-oxide

Richard D. Gilardi[a]* and Ray J. Butcher[b]

[a]Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375-5341, USA, and [b]Department of Chemistry, Howard University, 525 College Street, NW, Washington DC 20059, USA

Correspondence e-mail: gilardi@nrl.navy.mil

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.097
Data-to-parameter ratio = 11.3

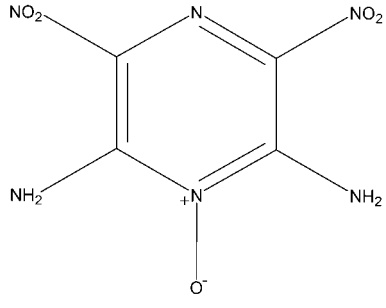
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_4H_4N_6O_5$, crystallizes in the monoclinic space group $P2_1/n$, and is an energetic compound containing only C, H, N, and O with a density of 1.919 Mg m^{-3}. Among other reasons, this remarkably high density is attributed to an extensive system of intra- and intermolecular hydrogen bonds which results in a packing scheme involving zigzag sheets.

Received 4 June 2001
Accepted 21 June 2001
Online 29 June 2001

Comment

The title compound, 2,6-diamino-3,5-dinitro-1,4-pyrazine 1-oxide (ANPZO), (I), is a very stable and relatively insensitive energetic material with a very high density of 1.919 Mg m^{-3}. Every H atom is involved in intramolecular hydrogen-bonding interactions to its neighboring O atom as well as participating in intermolecular interactions with adjoining molecules. Thus, it is related to other similar compounds, such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB; Cady & Larson, 1965; Kolb & Rizzo, 1979) and 2,6-diamino-3,5,-dinitropyrazine (ANPZ; Gilardi & George, 1984), which have a similar extensive system of intra- and intermolecular hydrogen-bonding interactions resulting in a sheet-like packing system, high densities (1.937 and 1.812 Mg m^{-3}, respectively), and relative insensitivity. These intermolecular hydrogen-bonding interactions result in ruffled parallel sheets in the [101] direction. One of the potentially useful features of ANPZO is its relative insensitivity. Sensitivity is often tested *via* the drop-height method, *i.e.* the height of the drop of a steel ball required to detonate the compound, with large values reflecting insensitivity. In such testing, the parent molecule, ANPZ (2,6-diamino-3,5-dinitro-1,4-pyrazine), has values which are so large they cannot be accurately measured, while ANPZO has a value of 117 cm (Pagoria, 2001). These values indicate that ANPZO is safer than other commonly used energetic compounds such as trinitrotoluene (80 cm) and HMX (32 cm). Fig. 1 shows the structure and labeling scheme for the title compound. Hydrogen-bonding metrical parameters are given in Table 1.



(I)

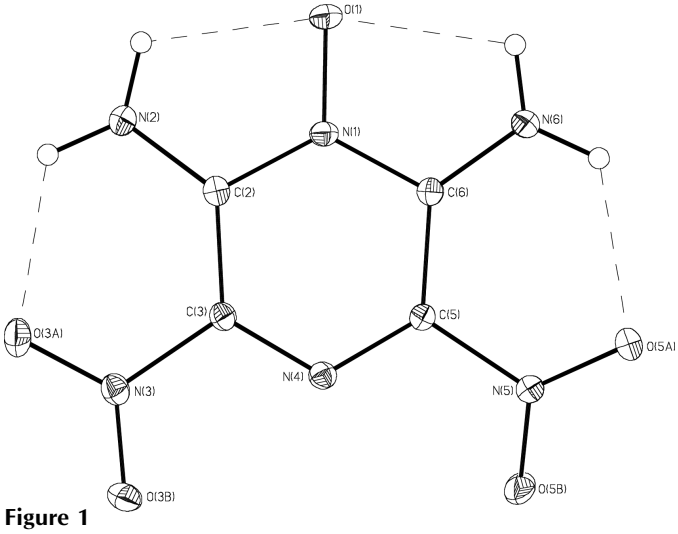


Figure 1
View of 2,6-diamino-3,5-dinitro-1,4-pyrazine 1-oxide showing the labeling of all non-H atoms. Displacement ellipsoids are at the 20% probability level. H atoms are drawn as small circles of arbitrary radii.

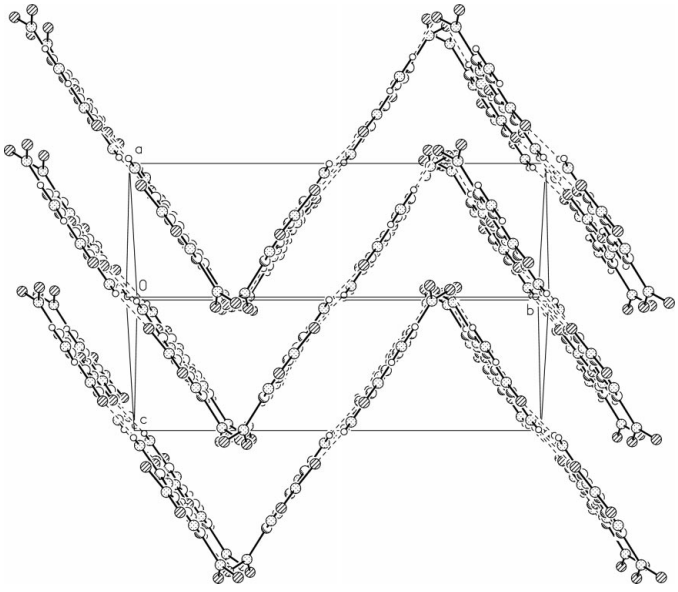


Figure 2
Packing diagram of 2,6-diamino-3,5-dinitro-1,4-pyrazine 1-oxide, viewed down the [101] direction.

Experimental

Crystals of the title compound were supplied by Dr Philip Pagoria, Energetic Materials Laboratory, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA. Crystal and reflection data were obtained using standard procedures (Butcher *et al.*, 1995).

Crystal data

$C_4H_4N_6O_5$
M_r = 216.13
Monoclinic, $P2_1/n$
a = 5.7159 (8) Å
b = 15.8498 (14) Å
c = 8.4139 (7) Å
β = 101.041 (7)°
V = 748.16 (14) Å^3
Z = 4
D_x = 1.919 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 58 reflections
θ = 2.8–18.3°
μ = 0.18 mm^{-1}
T = 294 (2) K
Chunky prism, yellow
0.40 × 0.30 × 0.25 mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
T_{min} = 0.990, T_{max} = 0.993
3771 measured reflections
1716 independent reflections
1185 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.5°
$h = 0 \rightarrow 7$
$k = -20 \rightarrow 18$
$l = -10 \rightarrow 10$
3 standard reflections
every 97 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.097
S = 1.01
1716 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0410P)^2 + 0.0834P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1^{i}	0.90 (2)	2.05 (2)	2.861 (2)	149 (2)
N2—H2A···O1	0.90 (2)	2.10 (2)	2.571 (2)	111.2 (18)
N2—H2B···O3A	0.93 (3)	2.08 (3)	2.697 (2)	123 (2)
N2—H2B···O3A^{ii}	0.93 (3)	2.36 (3)	3.224 (2)	154 (2)
N6—H6A···O5B^{iii}	0.91 (2)	2.10 (2)	2.974 (2)	160 (2)
N6—H6A···O5A	0.91 (2)	2.12 (2)	2.711 (2)	121.1 (18)
N6—H6A···N4^{iii}	0.91 (2)	2.69 (2)	3.189 (2)	114.9 (18)
N6—H6B···O3B^{iv}	0.90 (2)	2.51 (2)	3.115 (2)	125.0 (19)

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

Data collection: *XSCANS* (Bruker, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors wish to acknowledge the financial support from the Office of Naval Research, Mechanics Division. RJB wishes to acknowledge the ASEE/Navy Summer Faculty Research Program for support during the summer of 2001.

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