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2,6-Diamino-3,5-dinitropyrazine

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.064
wR factor = 0.187
Data-to-parameter ratio = 17.5

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

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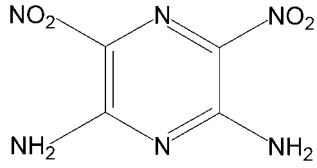
The title compound, $C_4H_4N_6O_4$, crystallizes in the monoclinic space group $P2_1/c$, and is an energetic compound containing only C, H, N and O atoms, with a density of 1.812 Mg m^{-3}. Thus, it is a very stable diaza analog of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Like TATB, it packs in planar graphite-like layers in the *ab* plane, with molecules held together by intermolecular hydrogen bonding. Both compounds decompose at temperatures above 573 K and are insoluble in most common solvents. Crystals of the title compound are usually twinned (twins related by a 180° rotation about *a**) and the crystal analyzed had a minor twin component.

Comment

The title compound, 2,6-diamino-3,5-dinitro-1,4-pyrazine (ANPZ), (I), is a very stable insensitive energetic material with a high density of 1.812 Mg m^{-3}. Thus, it is a very stable diaza analog of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).



(I)

In ANPZ, every H atom is either involved in intramolecular hydrogen-bonding interactions to a neighboring O atom or intermolecular hydrogen-bonding interactions with O atoms from adjoining molecules. This results in a packing scheme in which the molecules are strongly linked in two-dimensional planar graphite-like layers in the *ab* plane which stack along the *c* direction. Both ANPZ and TATB decompose at temperatures above 573 K and are insoluble in most common solvents. Crystals of the title compound are usually twinned (twins related by a 180° rotation about *a**) and the crystal analyzed had a minor twin component. It is related to other similar energetic compounds, such as TATB (TATB: Cady & Larson, 1965; Kolb & Rizzo, 1979) and 2,6-diamino-3,5-dinitropyrazine-1-oxide (ANPZO: Gilardi & Butcher, 2001) which have a similar system of extensive intra- and intermolecular hydrogen-bonding interactions, resulting in a sheet-like packing system, high densities (1.937 and 1.919 Mg m^{-3}, respectively), and relative insensitivity. One of the potentially useful features of ANPZ is its 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

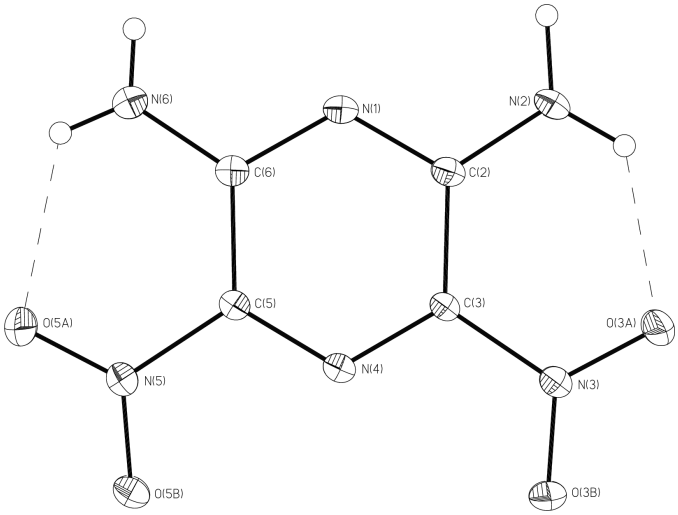


Figure 1
View of 2,6-diamino-3,5-dinitro-1,4-pyrazine showing the labeling of all non-H atoms. Displacement ellipsoids are at the 20% probability level; H atoms are drawn as small circles of arbitrary radii.

values reflecting insensitivity. In such testing, in common with TATB, the benchmark compound as regards insensitivity, ANPZ has values which are so large they cannot be accurately measured, while ANPZO has a value of 117 cm (Pagoria *et al.*, 1998). Thus, while the density of ANPZ is less than that of ANPZO, it is much less sensitive. Thus ANPZ is much 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.

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

$C_4H_4N_6O_4$
M_r = 200.13
Monoclinic, $P2_1/c$
a = 9.0136 (18) Å
b = 12.960 (6) Å
c = 6.3936 (13) Å
β = 100.77 (3)°
V = 733.7 (4) Å^3
Z = 4
D_x = 1.812 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 49 reflections
θ = 2.3–19.9°
μ = 0.16 mm^{-1}
T = 294 (2) K
Plate, yellow
0.35 × 0.28 × 0.12 mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
T_{min} = 0.943, T_{max} = 0.981
2526 measured reflections
2526 independent reflections
1715 reflections with $I > 2\sigma(I)$
θ_{max} = 25.5°
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -7 \rightarrow 7$
3 standard reflections
every 97 reflections
intensity decay: 1%

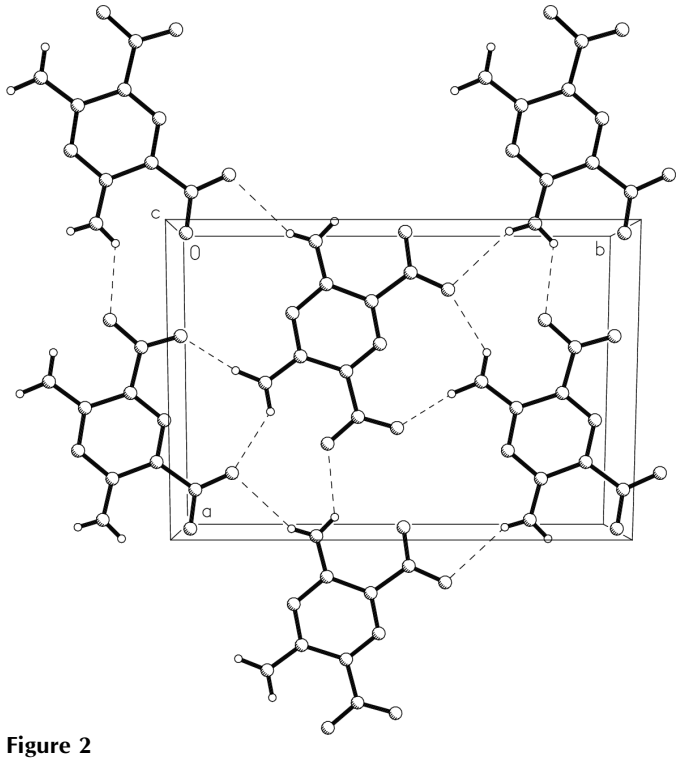


Figure 2
Packing diagram of 2,6-diamino-3,5-dinitro-1,4-pyrazine. Hydrogen bonds are indicated by dashed lines.

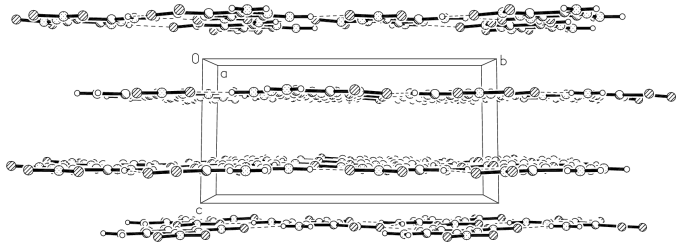


Figure 3
Packing diagram for 2,6-diamino-3,5-dinitro-1,4-pyrazine showing the parallel layers in the *bc* plane, viewed down the *a* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.187
S = 1.04
2526 reflections
144 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1032P)^2 + 0.2079P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···O3B^{i}	0.96 (3)	1.94 (3)	2.894 (4)	170 (2)
N2—H1···N4^{i}	0.96 (3)	2.64 (3)	3.253 (3)	122.0 (19)
N2—H2···O3A	0.89 (4)	1.98 (4)	2.644 (3)	130 (3)
N2—H2···O5B^{i}	0.89 (4)	2.25 (3)	2.973 (3)	138 (3)
N6—H3···O5A	0.81 (3)	2.11 (3)	2.667 (4)	125 (3)
N6—H3···O3A^{ii}	0.81 (3)	2.30 (3)	2.903 (3)	131 (3)
N6—H4···O5B^{iii}	0.79 (4)	2.50 (4)	3.219 (3)	153 (3)

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

Crystals of the title compound were all found to be twinned by a 180° rotation about a^*. This leads to near coincidence of $l = 2n$ ($n > 0$) reflections, complete separation of $l = 2n + 1$ reflections, and complete overlap of $l = 0$ reflections with reflections originating from the minor twin. It was found that the indices of coincident or almost coincident reflections were related by: $h_w = h_s + (l_s/2)$, $k_w = -k_s$ and $l_w = -l_s$, where w and s stand for weak and strong. This was handled by using the appropriate matrix with the *TWIN* instruction in *SHELXTL* (Sheldrick, 1997) and a scale factor for the minor component. After refinement the fraction of the minor component was found to be only 0.067 (2).

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

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