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2,6-Diamino-3,5-dinitro-1,4-pyrazine dimethyl sulfoxide solvate

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Key indicators

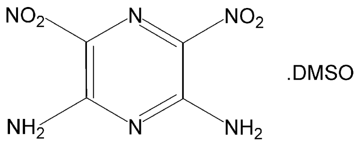
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.091
Data-to-parameter ratio = 12.9

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

The title compound, $C_4H_4N_6O_4 \cdot C_2H_6OS$, crystallizes in the triclinic space group $P\overline{1}$. It is a dimethyl sulfoxide (DMSO) solvate of the insensitive energetic compound 2,6-diamino-3,5-dinitro-1,4-pyrazine (ANPZ). The structure has been determined to obtain more accurate metrical parameters for the 2,6-diamino-3,5-dinitro-1,4-pyrazine moiety than those obtained from unsolvated crystals which are invariably twinned. The packing motif consists of two formula units linked by strong complementary hydrogen bonds between the ANPZ units with the two DMSO solvate molecules each linked by two bifurcated hydogen bonds to the two ANPZ units. This central motif is further linked into planar sheets by weaker interactions between the DMSO methyl H atoms and the O atoms from the nitro groups. This looser packing arrangement compared to ANPZ is reflected in a lower density (1.662 Mg m^{-3} *versus* 1.812 Mg m^{-3} for ANPZ).

Comment

The title compound, 2,6-diamino-3,5-dinitro-1,4-pyrazine dimethyl sulfoxide solvate, (I), is a dimethyl sulfoxide (DMSO) solvate of the insensitive energetic molecule 2,6-diamino-3,5-dinitro-1,4-pyrazine (ANPZ). ANPZ is a member of an important family of insensitive energetic compounds (TATB: Cady & Larson, 1965; Kolb & Rizzo, 1979; ANPZ: Gilardi & Butcher, 2001; ANPZO: Gilardi & Butcher, 2001), in which the molecules exhibit both multiple intramolecular and intermolecular hydrogen bonding interactions (TATB is 1,3,5-triamino-2,4,6-trinitrobenzene and ANPZO is 2,6-diamino-3,5-dinitropyrazine 1-oxide).



(I)

The intermolecular hydrogen-bonding interactions result in a planar sheet-like packing arrangement where the spacing between the layers resembles that of graphite. The significant feature of this family of energetic molecules is their 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, 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

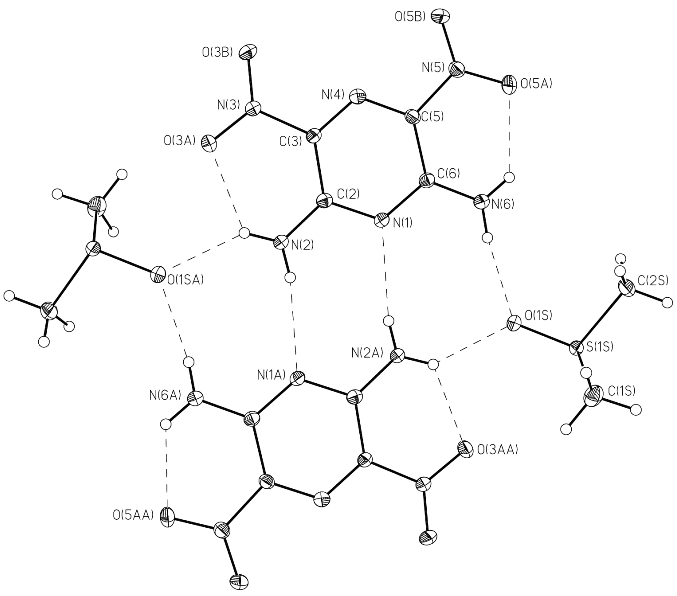


Figure 1

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

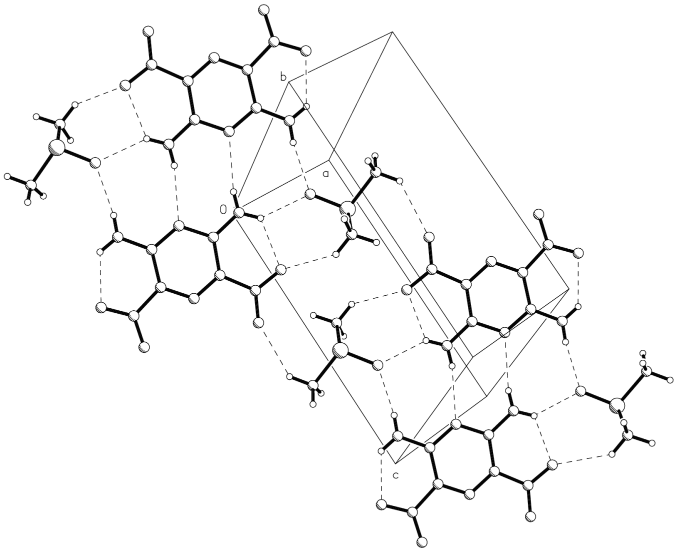


Figure 2

Packing diagram of 2,6-diamino-3,5-dinitro-1,4-pyrazine dimethyl sulfoxide solvate.

117 cm (Pagoria *et al.*, 1998). Thus ANPZ is much safer than other commonly used energetic compounds such as trinitrotoluene (80 cm) and HMX (32 cm). The primary motivating factor in determining the structure of the ANPZ solvate was to obtain more accurate metrical parameters for ANPZ as its crystals are invariably twinned (Gilardi & Butcher, 2001). The packing motif for the DMSO solvate consists of two ANPZ molecules linked by strong complementary hydrogen bonds and DMSO solvate molecules, each linked by two bifurcated hydrogen bonds to the ANPZ dimer. This central motif is further linked into planar sheets by weaker interactions between the DMSO methyl H atoms and the O atoms from the nitro groups. This packing arrangement is looser than that of ANPZ, and results in a lower density (1.662 Mg m^{-3} *versus* 1.812 Mg m^{-3} for ANPZ). Fig. 1 shows the structure and labeling scheme for the title compound, while Fig. 2 shows the packing arrangement. 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

$C_4H_4N_6O_4\cdot C_2H_6OS$
M_r = 278.26
Triclinic, $P\overline{1}$
a = 5.7817 (5) Å
b = 8.1353 (8) Å
c = 12.0270 (11) Å
α = 99.253 (2)°
β = 94.113 (2)°
γ = 92.482 (2)°
V = 556.04 (9) Å^3
Z = 2
D_x = 1.662 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3759 reflections
θ = 2.5–28.3°
μ = 0.32 mm^{-1}
T = 93 (2) K
Prism, yellow
0.65 × 0.22 × 0.07 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
$T_{\min}$ = 0.919, $T_{\max}$ = 0.969
4175 measured reflections
2638 independent reflections
2505 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 28.3°
$h = -6 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.14
2638 reflections
204 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.3143P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.006
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.005 (2)

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3A	0.83 (2)	2.10 (2)	2.6703 (18)	125.6 (17)
N2—H2A···O1S$^{\rm i}$	0.83 (2)	2.10 (2)	2.7884 (17)	139.9 (18)
N2—H2B···N1$^{\rm i}$	0.80 (2)	2.25 (2)	3.0407 (18)	170 (2)
N6—H6A···O5A	0.86 (2)	2.06 (2)	2.6831 (18)	128.8 (18)
N6—H6B···O1S	0.82 (2)	2.05 (2)	2.8541 (17)	171 (2)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$.

Data collection: *SMART* (Bruker, 1994); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1994); 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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