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1,5-Dimethyl-1,2,4,5-tetrazinane-3,6-dione

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Slight pyramidalization at the four N atoms leads to a twist boat conformation for the tetrazinane ring of the title compound, $C_4H_8N_4O_2$. In the crystal structure, the tetrazinane-3,6-dione molecules are disordered over two conformations with opposite ring puckerings, and are linked into two-dimensional sheets by N—H···O hydrogen bonding.

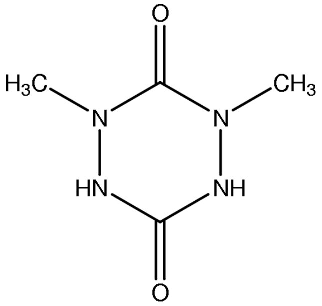
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–N) = 0.003 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.110
Data-to-parameter ratio = 11.2

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

Comment

In the search for molecule-based magnets, verdazyl radicals are viable ligands for the design of novel metal–radical assemblies (Hicks, 2001). We recently reported the preparation of the new chelating verdazyl ligand 1,5-dimethyl-3-(1-methyl-3-pyrazolyl)-6-oxoverdazyl (Meprv) and its ruthenium(II) complex, $[Ru(bpy)_2(Meprv)](BPh_4)_2$ (bpy is 2,2′-bipyridine (Wu *et al.*, 2003). In an attempt to recrystallize $prvH_3$, the hydrogenated precursor to Meprv, crystals of the title compound, (I), suitable for X-ray diffraction were unexpectedly obtained.


(I)

The tetrazinane-3,6-dione molecule is disordered over two conformations with opposite ring puckerings and relative occupancies of 0.729:0.271(9), as shown in Fig. 1. The major conformer is depicted in Fig. 2, and selected geometric parameters for this conformer are listed in Table 1. Owing to the slight pyramidalization at the four N atoms (Table 1), the tetrazinane ring is puckered, with an approximate C_2-symmetry axis through the two C atoms. The calculated puckering parameters of $Q = 0.493$ (2) Å, $\theta = 87.2$ (2)°, and $\varphi = 205.3$ (2)° are consistent with a twist–boat conformation (ideal values $\theta = 90°$ and $\varphi = 210°$; Cremer & Pople, 1975). The observed ring geometry, as well as the bond lengths and angles of (I) are comparable to those found in 1,2,4,5-tetramethyl-1,2,4,5-tetrazinane-3,6-dione (Nelsen *et al.*, 1991).

The crystal structure of (I) is composed of two-dimensional sheets of hydrogen-bonded tetrazinane-3,6-dione molecules (Fig. 3). Both amide groups of the tetrazinane ring participate

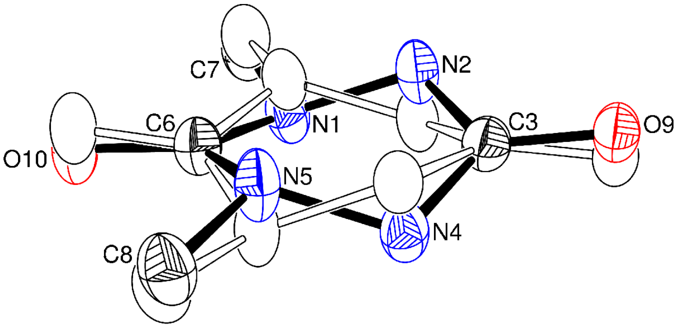


Figure 1
A view of the molecular structure of (I), showing the opposite ring puckerings of the two disordered conformers. The major conformer is coloured and labelled. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

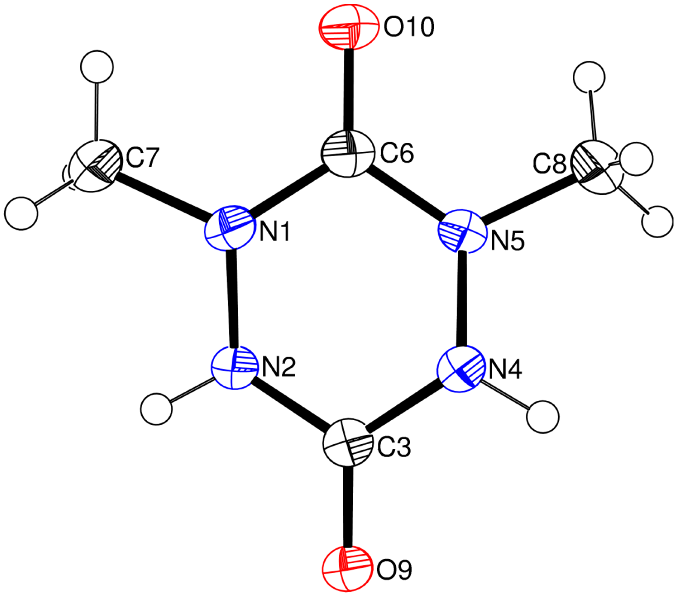


Figure 2
A view of the major ring conformer of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

in intermolecular N—H$\cdots$O interactions with the carboxyl O atoms of neighbouring molecules. Propagation of the N2—H2$\cdots$O10^{i} interaction leads to the formation of one-dimensional $C(5)$ chains along the [010] direction; the N4—H4$\cdots$O9^{ii} interaction, in an $R_2^2(8)$ ring pattern, links the chains into a two-dimensional network parallel to (102) [symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$]. Geometric parameters for the intermolecular hydrogen bonding between major conformers are presented in Table 2. Those for interactions involving the minor conformer are similar.

Experimental

The title compound, (I), was obtained as a by-product in the synthesis of 1,5-dimethyl-3-(3-pyrazolyl)-6-oxotetrazane (prvH$_3$; Wu *et al.*, 2003). Attempted recrystallization of prvH$_3$ from a mixture of methanol and ethyl acetate led instead to the isolation of colourless needles of (I) that were suitable for X-ray analysis. The compound may have been formed through the 1:1 reaction of methylhydrazine with triphosgene (Neugebauer *et al.*, 1983).

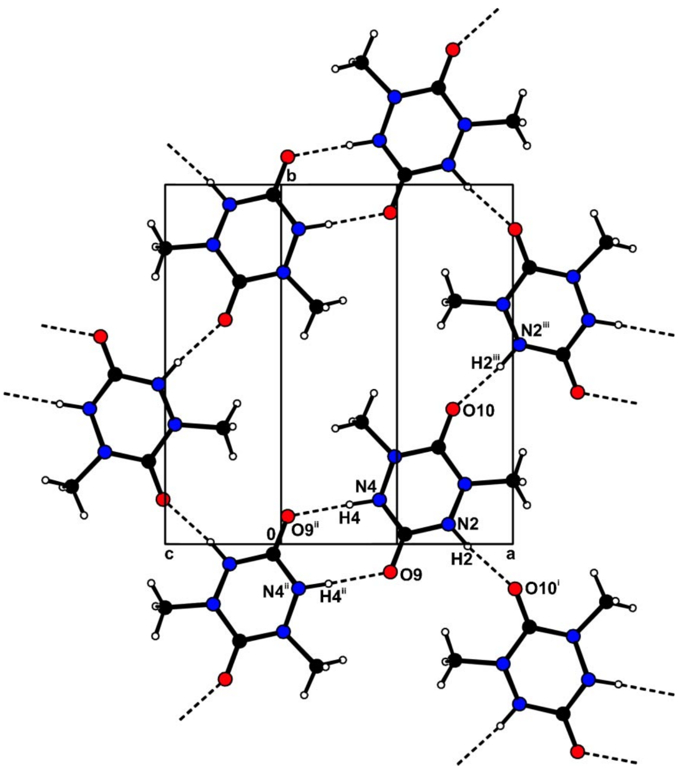


Figure 3
A view down [102] of part of the crystal structure of (I), showing a two-dimensional sheet of hydrogen-bonded tetrazinane-3,6-dione molecules [symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$; (iii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

Crystal data

$C_4H_8N_4O_2$
$M_r = 144.14$
Monoclinic, $P2_1/c$
$a = 7.6861\ (3)$ Å
$b = 10.8182\ (4)$ Å
$c = 7.8238\ (3)$ Å
$\beta = 91.4690\ (16)^\circ$
$V = 650.33\ (4)$ Å^3
$Z = 4$

$D_x = 1.472$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5956 reflections
$\theta = 1.0$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 150\ (2)$ K
Needle, colourless
0.27 × 0.27 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
6507 measured reflections
1482 independent reflections
1146 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\rm max} = 27.5^\circ$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 13$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.110$
$S = 1.05$
1482 reflections
132 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.0925P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °) for the major conformer of (I).

N1—N2	1.434 (3)	N4—N5	1.432 (2)
N1—C7	1.459 (3)	N5—C6	1.365 (2)
N2—C3	1.356 (2)	N5—C8	1.456 (3)
C3—N4	1.356 (2)	C6—N1	1.370 (3)
C3—O9	1.242 (3)	C6—O10	1.234 (3)
C6—N1—N2	116.6 (2)	C3—N4—N5	115.38 (17)
C6—N1—C7	120.7 (3)	N4—N5—C6	116.72 (19)
N2—N1—C7	112.4 (3)	N4—N5—C8	113.2 (3)
N1—N2—C3	117.30 (18)	C6—N5—C8	119.6 (3)
N2—C3—N4	114.89 (14)	N5—C6—N1	113.93 (16)
N2—C3—O9	120.9 (3)	N5—C6—O10	123.2 (3)
N4—C3—O9	124.2 (3)	N1—C6—O10	122.8 (3)

Table 2
Geometry (Å, °) of intermolecular hydrogen-bonding interactions between major conformers in (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O10^{i}	0.880 (14)	1.917 (15)	2.791 (4)	171.9 (18)
N4—H4···O9^{ii}	0.916 (14)	1.898 (15)	2.813 (6)	177.3 (19)

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

The initial solution for (I) consisted of a nearly planar tetrazinane-3,6-dione molecule containing unusually short N—N distances; however, a more reasonable ring geometry was obtained by splitting the four N positions into two partially occupied sites each. In subsequent refinements, (I) was modelled as being disordered over two conformations with opposite ring puckerings. The positions of the two ring C atoms were constrained to be identical in both conformers. In addition, all corresponding atoms (which are separated by distances of less than 0.6 Å) were constrained to have the same displacement parameters. The methyl H atoms were constrained to ideal geometries, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C—C bond. The positions of the H atoms bound to nitrogen were refined, with the N—H distances restrained to 0.91 (2) Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. The 1,2- and 1,3-distances of the two molecular conformations were restrained to be similar within standard deviations of 0.01 or 0.02 Å, respectively. The relative occupancies of the two conformers refined to 0.729:0.271 (9). No evidence of twinning was observed.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL*2000 (Otwinowski & Minor, 1997); data reduction: *HKL*2000; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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