

2-[1-(Hydroxyimino)ethyl]-2,5,5-trimethylperhydropyrimidine-butane-2,3-dione monooxime (1/1)

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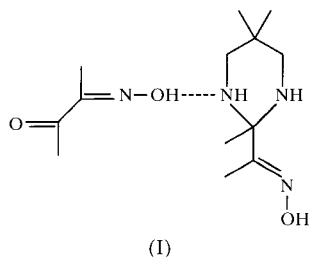
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The title compound, C₉H₁₉N₃O·C₄H₇NO₂, displays strong intramolecular O—H···N [O···N 2.6743 (13) Å] and N—H···N [N···N 2.6791 (15) Å] hydrogen bonds, and strong intermolecular O—H···N [O···N 2.7949 (15) Å] and N—H···O [N···O 3.0924 (16) Å] hydrogen bonds. This creates chains of perhydropyrimidine molecules, linked by hydrogen bonds. Each chain is linked to a partner chain, through hydrogen bonds to two butane-2,3-dione monooxime molecules, in a structure reminiscent of a ladder.

Comment

Some recently reviewed data shows that oximes, although being classical ligands (Chakravorty, 1974; Keeney *et al.*, 1984), display a variety of reactivity modes unusual even in the context of modern coordination chemistry (Kukushkin *et al.*, 1996, 1999; Costes *et al.*, 1997). As far as the redox conversions of oxime species are concerned, they can be either reduced or oxidized in metal-mediated reactions. We report here the structure of the 1:1 molecular complex, (I), of 2-[1-(hydroxyimino)ethyl]-2,5,5-trimethylperhydropyrimidine and butane-2,3-dione monooxime.



The structure of (I) has an asymmetric unit containing one 2-[1-(hydroxyimino)ethyl]-2,5,5-trimethylperhydropyrimidine

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fragment and one butane-2,3-dione monooxime fragment, as shown in Fig. 1. The torsion angles O2—N4—C12—C10 [−177.73 (11)°], O3—C10—C12—N4 [−174.18 (14)°] and C11—C10—C12—C13 [−174.25 (14)°] indicate that the butane-2,3-dione monooxime molecule is nearly planar. The conformation of the perhydropyrimidine molecule is defined by the torsion angles C3—N2—C4—C5 [−56.05 (14)°], C3—N3—C6—C5 [55.30 (14)°], C4—N2—C3—C1 [−69.57 (13)°] and C8—C5—C6—N3 [67.81 (14)°]. The perhydropyrimidine moiety adopts an aminal structure, with the six-membered ring in a chair conformation and the oxime fragment, C(CH₃)-NOH, appearing as an axial substituent.

The perhydropyrimidine molecules form hydrogen-bonded chains which run parallel to [100]. These chains are cross-linked along the [001] direction *via* hydrogen bonds involving the butane-2,3-dione monooxime moieties, forming a pattern reminiscent of a ladder (Fig. 2).

A major point of interest is the presence of a hydrogen contact between the equatorial H atom on the ring N2 atom and atom N1 of the axial oxime group (Fig. 1). This bond is rather weak, with an H···N1 (acceptor) separation of 2.37 (2) Å. However, this hydrogen bond locks the ring in a chair conformation, in which the side chain containing the oxime is axial and inhibits the rotation of the oxime substituent around the C1—C3 bond which, due to its length of 1.5366 (16) Å, must be considered as a single bond.

Another hydrogen bond is formed between atom O2 of the butane-2,3-dione monooxime molecule and the ring N2 atom. This bond, with an H···N2 (acceptor) separation of 1.77 (2) Å, is stronger than the intramolecular bond considered above (Ishida & Kashino, 1999; Lavender *et al.*, 1999).

Intermolecular hydrogen bonding occurs between the ring N2 atom and atom O3¹ of a symmetry-related butane-2,3-dione monooxime molecule [symmetry code: (i) 1 − x, 1 − y, 1 − z]. This bond is weak, with an H···N1 (acceptor)

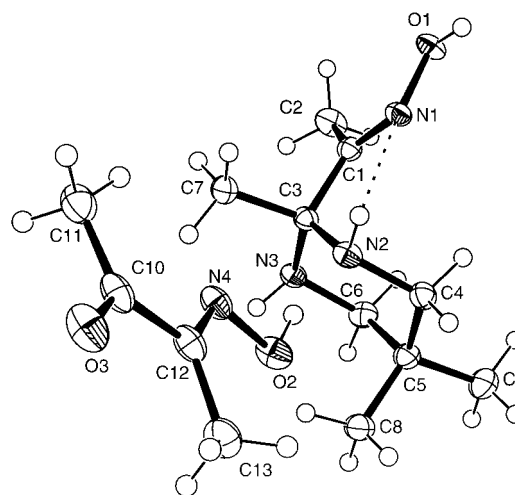


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and the dashed line indicates the N2—H···N1 intramolecular hydrogen bond.

separation of 2.25 (2) Å. It should be noted that considering the hydrogen bonds N2—H···N1, N2—H···O3ⁱ and O2—H···N2 would lead erroneously to the conclusion that N2 and N3 have distinctly different environments, when in fact these atoms are equivalent. This is reflected in the lengthening of the N2—C3 bond [1.4803 (14) Å] with respect to the N3—C3 bond [1.4654 (14) Å].

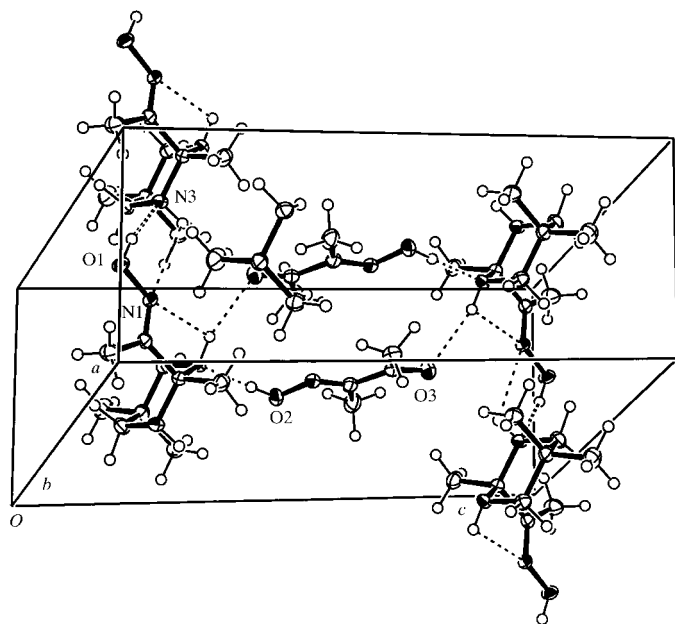


Figure 2
The unit-cell packing in (I). Dashed and double-dashed lines indicate hydrogen bonds.

C—H···N and C—H···O hydrogen bonds are also formed (Table 2). In the present study, the intra- and intermolecular hydrogen-bond lengths are comparable with the values found in related complexes (Steiner, 2000, 2001; Elerman *et al.*, 1998). The bond lengths and angles within the ring and oxime fragments compare well with those reported for a six-membered aminal (Fenton *et al.*, 1985; Raston *et al.*, 1978).

Experimental

Butane-2,3-dione monooxime (11.73 mmol) was dissolved in ethanol (200 ml), and a solution of 2,2-dimethyl-1,3-propanediamine (5.86 mmol) in ethanol (100 ml) was added dropwise. The resulting solution was refluxed for 2 h and then allowed to cool to room temperature. Colourless single crystals of (I) were obtained by slow evaporation.

Crystal data

C₉H₁₉N₃O·C₄H₇NO₂
M_r = 286.38
 Triclinic, *P*1
a = 6.4630 (3) Å
b = 8.3080 (5) Å
c = 16.3530 (9) Å
 α = 77.095 (3)°
 β = 86.747 (3)°
 γ = 67.554 (3)°
V = 790.65 (8) Å³

Z = 2
D_x = 1.203 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 9950 reflections
 θ = 0–27°
 μ = 0.09 mm⁻¹
T = 150 K
 Block, colourless
 0.6 × 0.4 × 0.4 mm

Data collection

Enraf–Nonius DIP2000 diffractometer
 ω scans
 Absorption correction: multi-scan (North *et al.*, 1968)
 T_{\min} = 0.950, T_{\max} = 0.965
 9950 measured reflections

2989 independent reflections
 2703 reflections with $I > 3\sigma(I)$
 R_{int} = 0.02
 θ_{max} = 26.6°
 h = 0 → 8
 k = -9 → 10
 l = -20 → 20

Refinement

Refinement on *F*
 R = 0.045
 wR = 0.048
 S = 0.94
 2703 reflections
 263 parameters
 All H-atom parameters refined

Weighting scheme: Chebyshev polynomial with 3 parameters (Carruthers & Watkin, 1979), 3.62 1.39 2.47
 $(\Delta/\sigma)_{\text{max}}$ = 0.006
 $\Delta\rho_{\text{max}}$ = 0.24 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.26 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—N1	1.4081 (12)	N3—C6	1.4740 (15)
O2—N4	1.3848 (13)	N4—C12	1.2879 (16)
O3—C10	1.2237 (16)	C1—C2	1.5010 (16)
N1—C1	1.2759 (16)	C3—C1	1.5366 (16)
N2—C3	1.4803 (14)	C5—C4	1.5301 (16)
N2—C4	1.4808 (15)	C5—C6	1.5286 (16)
N3—C3	1.4654 (14)	C10—C12	1.4930 (17)
O1—N1—C1	113.06 (9)	N2—C4—C5	111.8 (1)
C3—N2—C4	113.52 (8)	N3—C3—N2	110.88 (9)
C3—N3—C6	112.5 (1)	N3—C3—C1	110.26 (9)
O2—N4—C12	111.6 (1)	N3—C3—C7	107.9 (1)
N1—C1—C3	114.66 (9)	N3—C6—C5	113.85 (9)
N1—C1—C2	124.41 (11)	N4—C12—C10	115.69 (11)
N2—C3—C7	107.16 (9)	O3—C10—C11	121.16 (12)
N2—C3—C1	112.22 (9)	O3—C10—C12	118.67 (12)
C4—N2—C3—C1	-69.57 (13)	C8—C5—C6—N3	67.81 (14)
C3—N2—C4—C5	-56.05 (14)	O2—N4—C12—C10	-177.73 (11)
C6—N3—C3—C1	71.98 (12)	O3—C10—C12—N4	-176.18 (14)
C3—N3—C6—C5	55.30 (14)	C11—C10—C12—C13	-174.25 (14)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2···N1	0.88 (2)	2.37 (2)	2.6791 (15)	101 (1)
N2—H2···O3 ⁱ	0.88 (2)	2.25 (2)	3.0924 (16)	161 (1)
O1—H11···N3 ⁱⁱ	0.91 (3)	1.91 (2)	2.7949 (15)	162 (2)
O2—H21···N2	0.92 (2)	1.77 (2)	2.6743 (13)	168 (2)
C6—H61···O1 ⁱⁱⁱ	0.99 (2)	2.50 (2)	3.4377 (14)	159 (2)
C11—H111···N4	0.95 (2)	2.46 (2)	2.8115 (18)	102 (2)
C13—H131···O3	0.98 (2)	2.40 (2)	2.8162 (19)	105 (2)

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) 1 + *x*, *y*, *z*; (iii) 1 - *x*, 1 - *y*, -*z*.

H atoms were refined isotropically using full matrix least-squares [*C*—H = 0.95 (2)–1.02 (2) Å].

Data collection: DIP2000 software *DENZO* (Otwinowski & Minor, 1997); cell refinement: DIP2000 software *DENZO*; data reduction: DIP2000 software *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1033). Services for accessing these data are described at the back of the journal.

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