

1,4-Diazaspiro[4.5]decane-2,3-dione

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.046

wR factor = 0.106

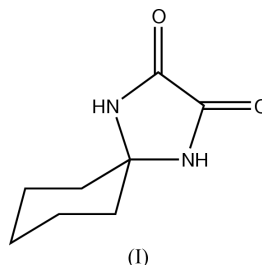
Data-to-parameter ratio = 17.9

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

The spirane 1,4-diazaspiro[4.5]decane-2,3-dione, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$, or 2,2-pentamethylene-4,5-imidazolidinedione, has been prepared and found to crystallize with two independent molecules in the asymmetric unit. Though nearly identical in geometry, the two distinct molecules undergo two different styles of co-operative hydrogen bonding, namely a planar and a canted arrangement.

Comment

As part of a research program concerning alternative methods for the synthesis of *gem*-bis(difluoramino)alkanes, we required the title compound, (I) (Davis, Chapman & Johnson, 2002). The 2,2-dialkyl-4,5-imidazolidinedione ring system is seldom encountered in the literature, in spite of a convenient method of preparation (Gruber & Dehler, 1971). Compound (I) was synthesized from cyclohexanone by the patented procedure. To our knowledge, this is the first structural determination of this heterocyclic ring system.



Crystals of (I) suitable for diffraction were grown from saturated acetonitrile solutions. There are two independent molecules in the asymmetric unit; these are effectively identical in geometry and bond distances (Fig. 1). The imidazolidinedione ring is planar in each molecule. The torsion angles within the five-membered rings range between $0.2 (2)$ and $1.3 (2)^\circ$. The cyclohexane rings adopt chair conformations. These features are similar to those observed in the crystal structure of the related heterocycle, 1 β -methyl-4 α -isopropylcyclohexyl-spiro-5'-hydantoin (Galdecki & Karolak-Wojciechowska, 1986).

The C—C bond lengths between the carbonyl groups appear anomalously long [$1.528 (2)$ and $1.521 (2) \text{ \AA}$], but this trait is mirrored in other structurally characterized oxamide derivatives (Chen *et al.*, 1991).

Both molecules within the asymmetric unit are involved in the hydrogen-bonding network (Fig. 2). One molecule forms a planar co-operative hydrogen-bonding arrangement [$\text{H}\cdots\text{O}$ $1.98 (1) \text{ \AA}$] with a symmetry-related amide group. The other portion of the dione, opposite this planar arrangement, links to the canted hydrogen-bonding network with one longer

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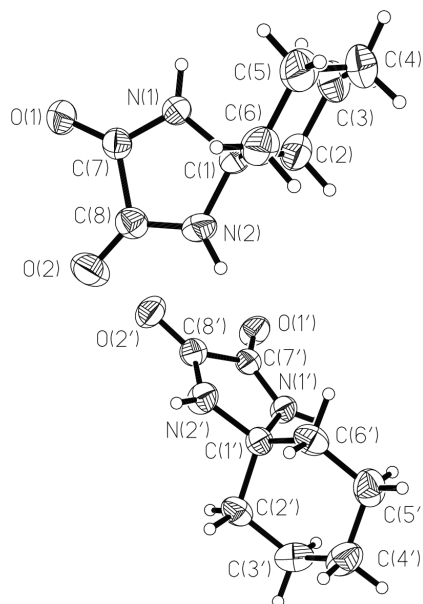


Figure 1
Drawing (SHELXTL; Bruker, 2000) of the title compound, illustrating the numbering scheme and showing displacement ellipsoids at the 50% probability level.

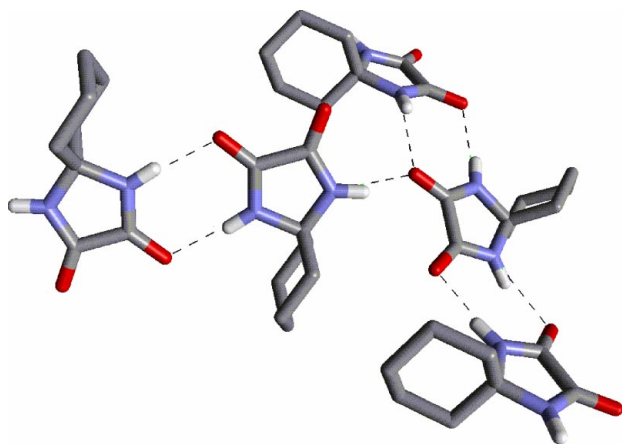


Figure 2
The hydrogen-bonding array in (I) (left: planar and right: canted)

hydrogen bond [$\text{H}\cdots\text{O}$ 2.06 (1) Å]. The infinite canted network is composed solely of the second molecule of the asymmetric unit. This co-operative network, with multiple hydrogen bonds between complementary functional groups, is analogous to that seen in the structurally similar 1,1-bisacetamidocyclohexane (Davis, Stasko & Chapman, 2002). The planes of the two imidazolidinediones are tilted by approximately 130 (1)°, resulting in a shallow herringbone arrangement, with hydrogen bonds between the amides [$\text{H}\cdots\text{O}$ 2.11 (1) Å].

Experimental

Cyanogen (7 ml) was collected in a graduated test tube cooled to 248 K, which was then stoppered by a septum. The tube was connected *via* Teflon tubing to a vigorously stirred mixture of cyclohexanone (10 g, 10.6 ml, 102 mmol) in 5% NaOH (75 ml, 94 mmol), and cooled in an ice bath. The 248 K bath was removed

and the Teflon tubing was immersed in the ketone mixture. After the cyanogen had bubbled through the reaction mixture (approximately 30 min), the tubing and the ice bath were removed, and the reaction mixture stirred for 24 h. The mixture was then cooled in an ice bath and neutralized with 50% H_2SO_4 , causing the product to precipitate. The mixture was filtered, the product washed with H_2O and then suction dried. The product was recrystallized from MeCN (4.7 g, 28%); m.p. 573 K (decomposition); ^1H NMR ($\text{DMSO}-d_6$): δ 9.98 (bs, 2H), 1.62–1.4 (m, 8H), 1.39–1.1 (m, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, p.p.m.): δ 159.65, 68.09, 38.30, 24.16, 21.90.

Crystal data

$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$
 $M_r = 168.20$
 Monoclinic, $P2_1/c$
 $a = 13.671$ (3) Å
 $b = 10.641$ (2) Å
 $c = 11.781$ (2) Å
 $\beta = 96.60$ (3)°
 $V = 1702.4$ (6) Å³
 $Z = 8$

$D_x = 1.312$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 18 reflections
 $\theta = 2$ –22.5°
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
 Rectangular prism, colorless
 0.5 × 0.5 × 0.2 mm

Data collection

Bruker P4 diffractometer
 ω scans
 4084 measured reflections
 3893 independent reflections
 2650 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 27.5^\circ$

$h = -17 \rightarrow 17$
 $k = -13 \rightarrow 0$
 $l = 0 \rightarrow 15$
 3 standard reflections
 every 48 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.107$
 $S = 1.04$
 3893 reflections
 217 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.4243P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1–N2	1.451 (2)	C1'–N2'	1.461 (2)
C1–N1	1.460 (2)	C1'–N1'	1.4650 (19)
C7–O1	1.2229 (19)	C7'–O1'	1.2271 (19)
C7–N1	1.327 (2)	C7'–N1'	1.318 (2)
C7–C8	1.528 (2)	C7'–C8'	1.521 (2)
C8–O2	1.211 (2)	C8'–O2'	1.2211 (19)
C8–N2	1.332 (2)	C8'–N2'	1.329 (2)
N2–C1–N1	100.50 (13)	N2'–C1'–N1'	99.78 (12)
N1–C7–C8	106.12 (14)	N1'–C7'–C8'	106.65 (14)
N2–C8–C7	104.89 (14)	N2'–C8'–C7'	104.77 (14)
C7–N1–C1	113.79 (13)	C7'–N1'–C1'	113.91 (13)
C8–N2–C1	114.68 (13)	C8'–N2'–C1'	114.79 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1–H1N ⁱ ⋯O1 ⁱ	0.86	1.98	2.8376 (19)	172
N2–H2N ⁱⁱ ⋯O1 ⁱⁱⁱ	0.86	2.06	2.7915 (19)	143
N1'–H1N' ⁱⁱⁱ ⋯O2 ⁱⁱⁱ	0.86	2.11	2.9561 (19)	167
N2'–H2N' ^{iv} ⋯O1 ^{iv}	0.86	2.13	2.8714 (19)	144

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

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, R., Rheingold, A. L. & Brill, T. B. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 173–177.
- Davis, M. C., Chapman, R. D. & Johnson, R. (2002). 223rd National Meeting of the American Chemical Society, Orlando, USA. Abstract FLUO 13.
- Davis, M. C., Stasko, D. & Chapman, R. D. (2002). *Synth. Commun.* Submitted.
- Galdecki, Z. & Karolak-Wojciechowska, J. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 467–474.
- Gruber, W. & Dehler, J. (1971). *Ger. Offen.* 2 018 433.
- Siemens (1994). *XSCANS*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.