

Crystal structure of 1-(piperidin-1-yl)-butane-1,3-dione

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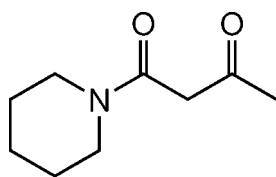
In the title compound, C₉H₁₅NO₂, the piperidine ring exhibits a chair conformation. The butanedione subunit exhibits a conformation with the ketone C atom in an eclipsed position with respect to the amide carbonyl group. In the crystal, a two-dimensional layered arrangement is formed by hydrogen bonds of the C—H...O type between the methyl group and the exocyclic methylene unit as donor sites and the amide carbonyl O atom as the acceptor of a bifurcated hydrogen bond. These layers are oriented parallel to the *ab* plane.

Keywords: crystal structure; 1-(piperidin-1-yl)butane-1,3-dione; weak hydrogen bonding.

CCDC reference: 1035958

1. Related literature

For the synthetic procedure, see: Sridharan *et al.* (2010). For a survey concerning weak hydrogen bonds, see: Desiraju & Steiner (1999).



2. Experimental

2.1. Crystal data

C₉H₁₅NO₂*M_r* = 169.22

Monoclinic, *P*2₁/*c*
a = 5.4455 (1) Å
b = 9.1901 (2) Å
c = 17.8837 (4) Å
 β = 94.506 (1)°
V = 892.22 (3) Å³

Z = 4
 Mo *K*α radiation
 μ = 0.09 mm⁻¹
T = 133 K
 0.12 × 0.09 × 0.07 mm

2.2. Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2002)
 T_{\min} = 0.717, T_{\max} = 0.746

5612 measured reflections
 2035 independent reflections
 1777 reflections with *I* > 2σ(*I*)
 R_{int} = 0.023

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
 $wR(F^2)$ = 0.107
 S = 1.14
 2035 reflections

169 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max}$ = 0.31 e Å⁻³
 $\Delta\rho_{\min}$ = -0.20 e Å⁻³

Table 1

Hydrogen-bond 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>
C7—H7B...O1 ⁱ	0.96 (2)	2.459 (17)	3.378 (3)	161 (1)
C9—H9B...O1 ⁱⁱ	0.99 (2)	2.601 (18)	3.466 (3)	146 (1)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BG2540).

References

- Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond*. Oxford University Press.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sridharan, V., Ruiz, M. & Menéndez, J. C. (2010). *Synthesis*, pp. 1053–1057.

supporting information

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Crystal structure of 1-(piperidin-1-yl)butane-1,3-dione

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S1. Comment

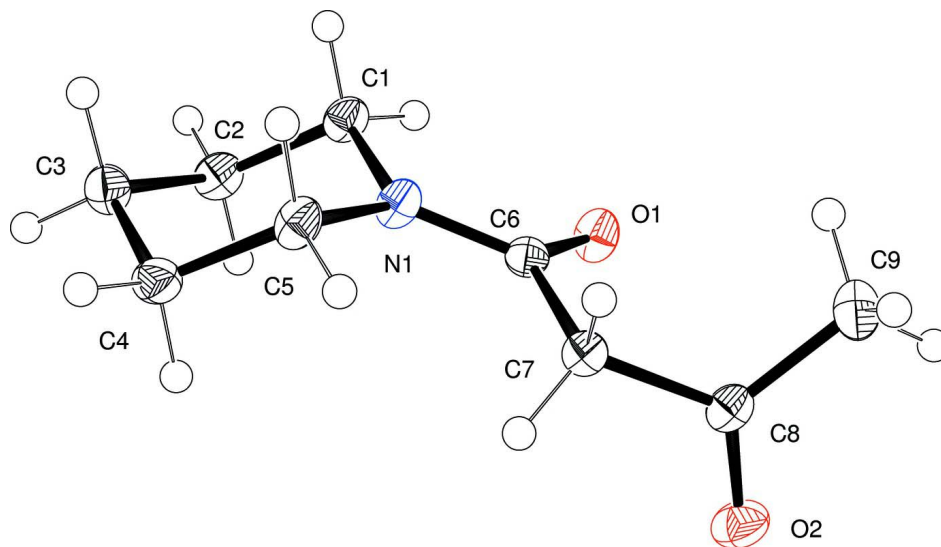
The title compound is an intermediate in the synthesis of 2,2-dimethoxy-1-(pyridin-2-yl)ethanone and has been synthesized from piperidine and 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one following a modified procedure (Sridharan *et al.*, 2010). As it is expected the piperidine ring shows a chair conformation and the amide substructure is planar. The butane-dione subunit exhibits a conformation with the ketone carbon atom in an eclipsed position with respect to the amide carbonyl group (Figure 1). The dihedral angle between the two carbonyl groups therefore measures to 81.4°. In the crystal structure, a two-dimensional layered arrangement is formed by hydrogen bonds of the C–H···O type between the methyl group and the exocyclic methylene unit as donor sites and the amide carbonyl oxygen atom as the acceptor of a bifurcated hydrogen bond. These layers are oriented along to the *ab* plane (Figure 2).

S2. Experimental

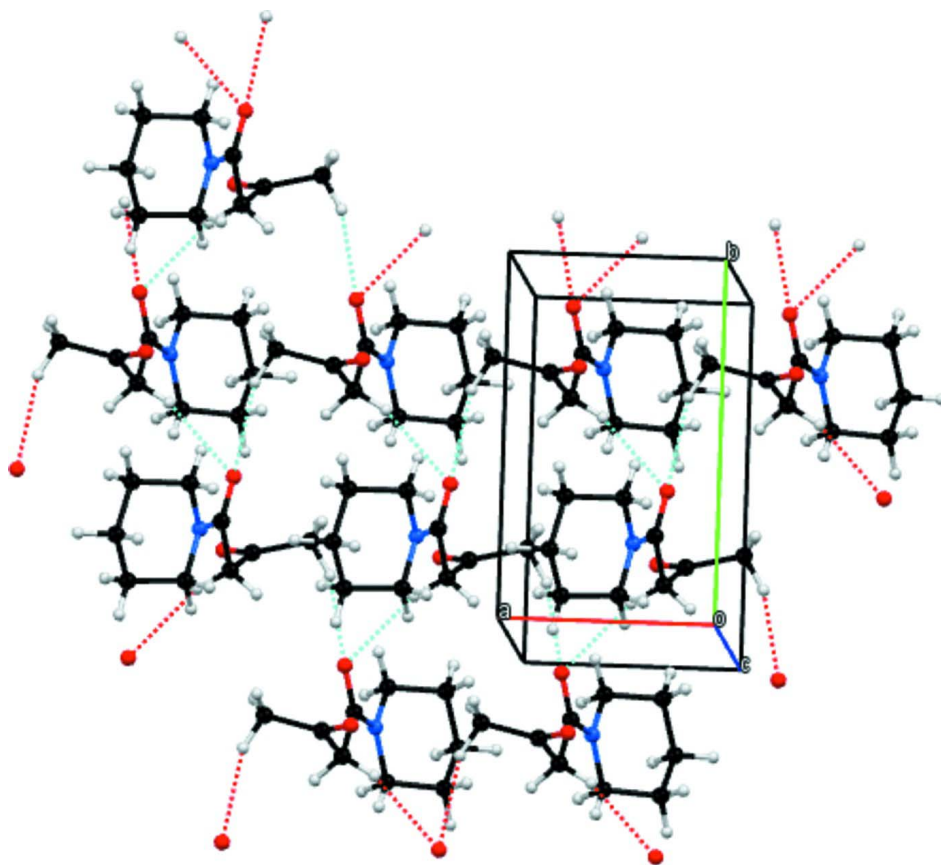
0.2 Mol of piperidine (17.0 g, 19.8 ml), 0.2 mol of sodium acetate (17.0 g) and a slight excess (0.26 mol, 37.0 g, 34.6 ml) 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one together with 40 ml THF are refluxed for 24 h. After cooling down to room temperature the solution is filtered and the remaining sodium acetate is washed with diethylether (3 × 20 ml). The combined THF and diethylether solutions are treated with brine (3 × 25 ml) and dried with Na₂SO₄. After filtration the organic solution is evaporated to dryness. The raw product may either be purified by chromatography (silica, light petroleum: ethyl acetate = 9: 1, yield 67%) or by distillation *in vacuo* (0.2 mbar, yield: 83%). If only the product fraction that is condensed into a Schlenk tube which is cooled with liquid nitrogen using a bath temperature above 100°C is collected, crystalline material of the title compound suitable for X-ray crystallography is obtained.

S3. Refinement

The positions of all hydrogen atoms have been determined from a Fourier map and all hydrogen atoms were refined without any constraints.

**Figure 1**

Molecular structure of the title compound with thermal ellipsoids drawn at the 50% probability level.

**Figure 2**

Crystal structure of the title compound showing layers of molecules along the *ab* plane which are built up by bifurcated C-H...O hydrogen bonds.

1-(Piperidin-1-yl)butane-1,3-dione*Crystal data*

C₉H₁₅NO₂
M_r = 169.22
 Monoclinic, *P*2₁/*c*
 Hall symbol: -*P* 2ybc
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c = 17.8837 (4) Å
 β = 94.506 (1)°
V = 892.22 (3) Å³

Z = 4
F(000) = 368
D_x = 1.260 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 μ = 0.09 mm⁻¹
T = 133 K
 Prism, colourless
 0.12 × 0.09 × 0.07 mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ϕ - ω -scan
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2002)
T_{min} = 0.717, *T_{max}* = 0.746

5612 measured reflections
 2035 independent reflections
 1777 reflections with *I* > 2σ(*I*)
R_{int} = 0.023
 θ_{\max} = 27.5°, θ_{\min} = 2.3°
h = -7→6
k = -7→11
l = -23→21

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.040
 $wR(F^2)$ = 0.107
S = 1.14
 2035 reflections
 169 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.4171P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of *F*² against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on *F*², conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative *F*². The threshold expression of *F*² > σ(*F*²) is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on *F*² are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
O1	0.73273 (18)	0.88779 (10)	0.27173 (5)	0.0232 (2)
O2	0.6753 (2)	0.70560 (11)	0.11035 (5)	0.0279 (3)
N1	0.5948 (2)	0.73198 (12)	0.35732 (6)	0.0202 (3)
C1	0.5498 (3)	0.84895 (15)	0.41067 (7)	0.0210 (3)
H1B	0.661 (3)	0.8308 (18)	0.4570 (9)	0.022 (4)*

H1A	0.594 (3)	0.9416 (19)	0.3881 (9)	0.023 (4)*
C2	0.2840 (3)	0.84538 (15)	0.43124 (8)	0.0236 (3)
H2B	0.257 (3)	0.9213 (19)	0.4687 (10)	0.027 (4)*
H2A	0.175 (3)	0.868 (2)	0.3865 (11)	0.032 (5)*
C3	0.2232 (3)	0.69623 (16)	0.46223 (8)	0.0236 (3)
H3A	0.331 (3)	0.6804 (19)	0.5103 (10)	0.027 (4)*
H3B	0.049 (4)	0.6953 (19)	0.4749 (10)	0.032 (5)*
C4	0.2753 (3)	0.57716 (16)	0.40620 (8)	0.0230 (3)
H4B	0.166 (3)	0.588 (2)	0.3604 (10)	0.033 (5)*
H4A	0.245 (3)	0.4812 (19)	0.4270 (9)	0.027 (4)*
C5	0.5391 (3)	0.58557 (14)	0.38390 (8)	0.0212 (3)
H5B	0.657 (3)	0.5641 (18)	0.4283 (9)	0.021 (4)*
H5A	0.565 (3)	0.5139 (19)	0.3448 (9)	0.023 (4)*
C6	0.6852 (2)	0.76255 (14)	0.29111 (7)	0.0170 (3)
C7	0.7267 (2)	0.63574 (14)	0.23861 (7)	0.0180 (3)
H7B	0.575 (3)	0.5836 (18)	0.2286 (9)	0.022 (4)*
H7A	0.854 (3)	0.5704 (19)	0.2607 (9)	0.024 (4)*
C8	0.8154 (2)	0.69439 (14)	0.16614 (7)	0.0190 (3)
C9	1.0830 (3)	0.73141 (18)	0.16694 (9)	0.0270 (3)
H9C	1.137 (4)	0.780 (2)	0.2127 (12)	0.046 (6)*
H9B	1.177 (4)	0.639 (2)	0.1650 (12)	0.049 (6)*
H9A	1.116 (4)	0.784 (2)	0.1229 (13)	0.053 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0316 (5)	0.0149 (5)	0.0240 (5)	0.0001 (4)	0.0072 (4)	0.0018 (4)
O2	0.0346 (6)	0.0292 (6)	0.0191 (5)	-0.0014 (4)	-0.0030 (4)	0.0028 (4)
N1	0.0295 (6)	0.0133 (5)	0.0183 (5)	-0.0003 (4)	0.0048 (4)	-0.0007 (4)
C1	0.0284 (7)	0.0164 (6)	0.0183 (6)	-0.0016 (5)	0.0035 (5)	-0.0030 (5)
C2	0.0285 (7)	0.0198 (7)	0.0226 (7)	0.0029 (5)	0.0024 (5)	-0.0021 (5)
C3	0.0231 (7)	0.0237 (7)	0.0244 (7)	-0.0008 (5)	0.0040 (5)	-0.0001 (5)
C4	0.0269 (7)	0.0208 (7)	0.0209 (7)	-0.0043 (5)	-0.0007 (5)	0.0003 (5)
C5	0.0309 (7)	0.0144 (6)	0.0188 (6)	-0.0006 (5)	0.0042 (5)	0.0020 (5)
C6	0.0167 (6)	0.0164 (6)	0.0176 (6)	0.0011 (5)	-0.0006 (5)	0.0005 (5)
C7	0.0200 (6)	0.0156 (6)	0.0183 (6)	0.0004 (5)	0.0015 (5)	0.0000 (5)
C8	0.0249 (7)	0.0142 (6)	0.0183 (6)	0.0023 (5)	0.0032 (5)	-0.0013 (5)
C9	0.0238 (7)	0.0298 (8)	0.0281 (8)	0.0013 (6)	0.0076 (6)	0.0033 (6)

Geometric parameters (Å, °)

O1—C6	1.2353 (16)	C4—C5	1.523 (2)
O2—C8	1.2117 (17)	C4—H4B	0.980 (18)
N1—C6	1.3472 (17)	C4—H4A	0.976 (18)
N1—C5	1.4667 (16)	C5—H5B	1.001 (16)
N1—C1	1.4706 (16)	C5—H5A	0.978 (17)
C1—C2	1.521 (2)	C6—C7	1.5244 (18)
C1—H1B	1.001 (16)	C7—C8	1.5171 (18)

C1—H1A	0.981 (17)	C7—H7B	0.959 (17)
C2—C3	1.525 (2)	C7—H7A	0.976 (17)
C2—H2B	0.987 (18)	C8—C9	1.496 (2)
C2—H2A	0.981 (19)	C9—H9C	0.96 (2)
C3—C4	1.525 (2)	C9—H9B	0.99 (2)
C3—H3A	1.012 (17)	C9—H9A	0.95 (2)
C3—H3B	0.993 (19)		
C6—N1—C5	125.13 (11)	H4B—C4—H4A	107.2 (14)
C6—N1—C1	120.59 (11)	N1—C5—C4	110.79 (11)
C5—N1—C1	114.27 (10)	N1—C5—H5B	107.6 (9)
N1—C1—C2	110.57 (11)	C4—C5—H5B	110.1 (9)
N1—C1—H1B	107.1 (9)	N1—C5—H5A	110.0 (10)
C2—C1—H1B	108.7 (9)	C4—C5—H5A	110.2 (9)
N1—C1—H1A	108.0 (10)	H5B—C5—H5A	108.2 (13)
C2—C1—H1A	112.9 (9)	O1—C6—N1	122.69 (12)
H1B—C1—H1A	109.4 (13)	O1—C6—C7	119.67 (12)
C1—C2—C3	110.19 (11)	N1—C6—C7	117.64 (11)
C1—C2—H2B	110.2 (10)	C8—C7—C6	109.09 (10)
C3—C2—H2B	109.9 (10)	C8—C7—H7B	110.2 (10)
C1—C2—H2A	108.8 (11)	C6—C7—H7B	109.2 (10)
C3—C2—H2A	110.9 (11)	C8—C7—H7A	107.6 (10)
H2B—C2—H2A	106.8 (14)	C6—C7—H7A	110.8 (10)
C2—C3—C4	110.44 (12)	H7B—C7—H7A	109.9 (14)
C2—C3—H3A	108.1 (10)	O2—C8—C9	122.56 (13)
C4—C3—H3A	109.2 (10)	O2—C8—C7	120.78 (12)
C2—C3—H3B	109.2 (10)	C9—C8—C7	116.62 (12)
C4—C3—H3B	111.9 (10)	C8—C9—H9C	110.5 (13)
H3A—C3—H3B	107.8 (14)	C8—C9—H9B	108.1 (12)
C5—C4—C3	111.32 (11)	H9C—C9—H9B	107.5 (18)
C5—C4—H4B	107.5 (11)	C8—C9—H9A	110.6 (13)
C3—C4—H4B	110.3 (11)	H9C—C9—H9A	113.9 (18)
C5—C4—H4A	109.8 (10)	H9B—C9—H9A	105.9 (18)
C3—C4—H4A	110.6 (10)		

Hydrogen-bond 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>
C7—H7B...O1 ⁱ	0.96 (2)	2.459 (17)	3.378 (3)	161 (1)
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