

4-Methyl-2-oxo-2,3,4,5-tetrahydro-1H-1,5-benzodiazepine-5-carbaldehyde

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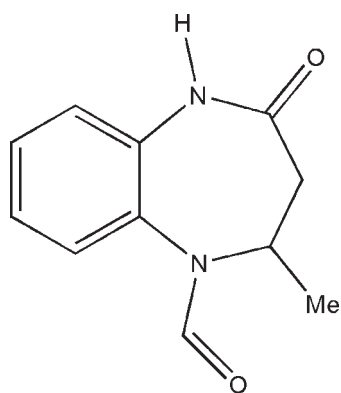
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.055; wR factor = 0.163; data-to-parameter ratio = 26.4.

In the title compound, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$, a benzodiazepine derivative, the seven-membered ring adopts a distorted boat conformation. The crystal packing is controlled by intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For the hypnotic effects of benzodiazepines, see: Gringauz (1999). For their use in the treatment of gastrointestinal and central nervous system disorders, see: Rahbaek *et al.* (1999). For other therapeutic applications, see: Albright *et al.* (1998); Lee *et al.* (1999). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For puckering and asymmetry parameters, see: Cremer & Pople (1975); ; Nardelli (1983). For details of the preparation, see: Venkatraj *et al.* (2008).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$ $b = 12.9387$ (4) Å
 $M_r = 204.23$ $c = 14.6227$ (5) Å
 Monoclinic, $P2_1/c$ $\beta = 97.968$ (2)°
 $a = 5.3284$ (1) Å $V = 998.39$ (5) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹

$T = 293$ K
 $0.30 \times 0.20 \times 0.15$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{\text{min}} = 0.977$, $T_{\text{max}} = 0.986$
 14697 measured reflections
 3727 independent reflections
 2453 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.163$
 $S = 1.05$
 3727 reflections
 141 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.89 (2)	2.12 (2)	2.9745 (16)	161.3 (18)
$\text{C13}-\text{H13}\cdots\text{O1}^{\text{ii}}$	0.93	2.38	3.2220 (18)	150

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5041).

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supplementary materials

Acta Cryst. (2009). E65, o2362 [doi:10.1107/S1600536809034825]

4-Methyl-2-oxo-2,3,4,5-tetrahydro-1H-1,5-benzodiazepine-5-carbaldehyde

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Comment

Benzodiazepines are used for the purpose of hypnotic effects, owing to their less toxic and less severe withdrawal effects when compared with barbiturates (Gringauz, 1999). Benzodiazepines from *aspergillus* include *asperlicin*, which is used for treatment of gastrointestinal and central nervous system (CNS) disorders (Rahbaek *et al.*, 1999). The other therapeutic applications (Lee *et al.*, 1999) of benzodiazepines include vasopressin antagonists (Albright *et al.*, 1998). In view of these importance and to ascertain the molecular conformation, crystallographic study of the title compound has been carried out.

The ORTEP diagram of the title compound is shown in Fig.1. The benzodiazepine ring adopts a distorted boat conformation. The puckering parameters (Cremer & Pople, 1975) and the asymmetry parameters (Nardelli, 1983) for this ring are $q_2 = 0.933(1) \text{ \AA}$, $q_3 = 0.170(1) \text{ \AA}$, $\varphi_2 = 144.8(1)^\circ$, $\varphi_3 = 18.0(4)^\circ$ and $\Delta 2(C4) = 13.2(1)^\circ$. The sum of the bond angles at N1(359.8°) and N5(359.8°) of the benzodiazepine ring is in accordance with sp^2 hybridization.

The crystal packing is controlled by N—H \cdots O and C—H \cdots O types of intermolecular interactions in addition to van der Waals forces. Atom N1 at (x, y, z) donates a proton to O2 $(1 - x, 1/2 + y, 1/2 - z)$, which forms a C7 (Bernstein *et al.*, 1995) one dimensional chain running along b-axis. The intermolecular hydrogen bond C13—H13 \cdots O1 also connects the molecule into another C7 chain running along b-axis. Thus the combination of N—H \cdots O and C—H \cdots O intermolecular hydrogen bonds form a graph set motif of $R_2^2(7)$ dimer to stabilize the molecules and extend along b-axis (Fig. 2).

Experimental

An ice-cold solution of acetic-formic anhydride was prepared from acetic anhydride (10 ml) and 85% formic acid (5 ml) was added slowly to a cold solution of tetrahydrobenzodiazepin-2-one (0.88 g) in anhydrous benzene (30 ml). The reaction mixture was stirred at room temperature for 4 hrs. The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated. The resulting mass was purified by crystallization from benzene-petroleum ether (333–353° K) mixture (1:1) (Venkatraj *et al.*, 2008)

Refinement

The H atom bonded to N was freely refined whereas the other H atoms were positioned geometrically (C—H=0.93–0.98 Å) and allowed to ride on their parent atoms, with $1.5U_{eq}(C)$ for methyl H and $1.2 U_{eq}(C)$ for other H atoms.

Figures

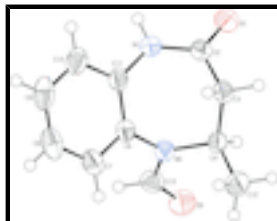


Fig. 1. Perspective view of the molecule showing the thermal ellipsoids are drawn at 50% probability level.

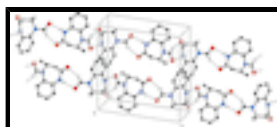


Fig. 2. The crystal packing of the molecules viewed down *a*-axis. H atoms not involved in hydrogen bonding have been omitted for clarity.

4-Methyl-2-oxo-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine-5-carbaldehyde

Crystal data

$C_{11}H_{12}N_2O_2$

$M_r = 204.23$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 5.32840\ (10)\ \text{\AA}$

$b = 12.9387\ (4)\ \text{\AA}$

$c = 14.6227\ (5)\ \text{\AA}$

$\beta = 97.968\ (2)^\circ$

$V = 998.39\ (5)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 432$

$D_x = 1.359\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2563 reflections

$\theta = 2.1\text{--}32.9^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.30 \times 0.20 \times 0.15\ \text{mm}$

Data collection

Bruker Kappa APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

ω and φ scans

Absorption correction: Multi-scan (SADABS; Sheldrick, 2001)

$T_{\min} = 0.977$, $T_{\max} = 0.986$

14697 measured reflections

3727 independent reflections

2453 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 32.9^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -8 \rightarrow 8$

$k = -19 \rightarrow 19$

$l = -22 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of

	independent and constrained refinement
$wR(F^2) = 0.163$	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.1596P]$
	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\max} = 0.004$
3727 reflections	$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
141 parameters	$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.5676 (2)	0.55730 (10)	0.36634 (8)	0.0596 (3)
O2	0.4734 (2)	0.15716 (8)	0.36319 (8)	0.0498 (3)
N1	0.3101 (2)	0.49320 (9)	0.24515 (8)	0.0411 (3)
H1	0.395 (4)	0.5303 (15)	0.2083 (14)	0.060 (5)*
C2	0.3797 (3)	0.50642 (10)	0.33737 (10)	0.0391 (3)
C3	0.2127 (3)	0.45788 (10)	0.39982 (9)	0.0370 (3)
H3A	0.0372	0.4725	0.3762	0.044*
H3B	0.2490	0.4889	0.4606	0.044*
C4	0.2483 (2)	0.34179 (10)	0.40847 (8)	0.0320 (3)
H4	0.4214	0.3286	0.4385	0.038*
N5	0.22002 (19)	0.29427 (8)	0.31600 (7)	0.0319 (2)
C6	0.0534 (2)	0.33715 (10)	0.24086 (8)	0.0313 (3)
C7	-0.1530 (3)	0.27966 (12)	0.19987 (10)	0.0421 (3)
H7	-0.1912	0.2168	0.2256	0.051*
C8	-0.3011 (3)	0.31534 (14)	0.12141 (11)	0.0522 (4)
H8	-0.4377	0.2764	0.0938	0.063*
C9	-0.2459 (3)	0.40821 (15)	0.08435 (11)	0.0552 (4)
H9	-0.3435	0.4315	0.0306	0.066*
C10	-0.0470 (3)	0.46775 (12)	0.12580 (10)	0.0479 (4)
H10	-0.0138	0.5315	0.1006	0.057*
C11	0.1037 (2)	0.43294 (10)	0.20486 (9)	0.0343 (3)
C12	0.0669 (3)	0.29350 (14)	0.46723 (11)	0.0503 (4)
H12A	-0.1043	0.3047	0.4387	0.075*
H12B	0.0909	0.3245	0.5274	0.075*

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H12C	0.0990	0.2206	0.4728	0.075*
C13	0.3356 (3)	0.20421 (10)	0.30322 (10)	0.0388 (3)
H13	0.3090	0.1754	0.2444	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0699 (7)	0.0577 (7)	0.0464 (7)	-0.0305 (6)	-0.0085 (5)	0.0062 (5)
O2	0.0557 (6)	0.0390 (5)	0.0529 (7)	0.0129 (4)	0.0013 (5)	0.0044 (5)
N1	0.0551 (7)	0.0357 (6)	0.0325 (6)	-0.0110 (5)	0.0055 (5)	0.0007 (5)
C2	0.0496 (7)	0.0299 (6)	0.0359 (7)	-0.0042 (5)	-0.0012 (5)	0.0001 (5)
C3	0.0445 (7)	0.0363 (6)	0.0298 (6)	0.0006 (5)	0.0036 (5)	-0.0063 (5)
C4	0.0333 (5)	0.0362 (6)	0.0259 (5)	-0.0012 (4)	0.0019 (4)	-0.0012 (5)
N5	0.0358 (5)	0.0295 (5)	0.0297 (5)	0.0016 (4)	0.0026 (4)	-0.0011 (4)
C6	0.0319 (5)	0.0347 (6)	0.0269 (6)	0.0025 (4)	0.0027 (4)	-0.0038 (5)
C7	0.0389 (7)	0.0466 (8)	0.0404 (7)	-0.0060 (5)	0.0034 (5)	-0.0092 (6)
C8	0.0389 (7)	0.0694 (10)	0.0453 (8)	0.0016 (7)	-0.0052 (6)	-0.0185 (8)
C9	0.0544 (9)	0.0720 (11)	0.0348 (7)	0.0229 (8)	-0.0100 (6)	-0.0063 (7)
C10	0.0634 (9)	0.0443 (8)	0.0337 (7)	0.0138 (7)	-0.0012 (6)	0.0021 (6)
C11	0.0407 (6)	0.0338 (6)	0.0278 (6)	0.0033 (5)	0.0027 (5)	-0.0041 (5)
C12	0.0563 (9)	0.0571 (9)	0.0397 (8)	-0.0147 (7)	0.0142 (6)	0.0001 (7)
C13	0.0428 (7)	0.0298 (6)	0.0436 (7)	0.0026 (5)	0.0055 (5)	-0.0019 (5)

Geometric parameters (\AA , $^\circ$)

O1—C2	1.2240 (16)	C6—C11	1.3872 (18)
O2—C13	1.2248 (17)	C6—C7	1.3925 (17)
N1—C2	1.3589 (18)	C7—C8	1.379 (2)
N1—C11	1.4088 (17)	C7—H7	0.9300
N1—H1	0.89 (2)	C8—C9	1.367 (3)
C2—C3	1.498 (2)	C8—H8	0.9300
C3—C4	1.5170 (18)	C9—C10	1.381 (2)
C3—H3A	0.9700	C9—H9	0.9300
C3—H3B	0.9700	C10—C11	1.3881 (18)
C4—N5	1.4740 (16)	C10—H10	0.9300
C4—C12	1.5145 (19)	C12—H12A	0.9600
C4—H4	0.9800	C12—H12B	0.9600
N5—C13	1.3430 (16)	C12—H12C	0.9600
N5—C6	1.4259 (15)	C13—H13	0.9300
C2—N1—C11	125.06 (12)	C8—C7—C6	120.40 (14)
C2—N1—H1	116.2 (13)	C8—C7—H7	119.8
C11—N1—H1	118.5 (13)	C6—C7—H7	119.8
O1—C2—N1	120.58 (14)	C9—C8—C7	119.65 (14)
O1—C2—C3	122.74 (13)	C9—C8—H8	120.2
N1—C2—C3	116.67 (12)	C7—C8—H8	120.2
C2—C3—C4	112.83 (11)	C8—C9—C10	120.70 (14)
C2—C3—H3A	109.0	C8—C9—H9	119.6
C4—C3—H3A	109.0	C10—C9—H9	119.6

C2—C3—H3B	109.0	C9—C10—C11	120.32 (15)
C4—C3—H3B	109.0	C9—C10—H10	119.8
H3A—C3—H3B	107.8	C11—C10—H10	119.8
N5—C4—C12	110.87 (11)	C6—C11—C10	119.08 (13)
N5—C4—C3	109.94 (10)	C6—C11—N1	121.10 (11)
C12—C4—C3	111.93 (12)	C10—C11—N1	119.78 (13)
N5—C4—H4	108.0	C4—C12—H12A	109.5
C12—C4—H4	108.0	C4—C12—H12B	109.5
C3—C4—H4	108.0	H12A—C12—H12B	109.5
C13—N5—C6	118.62 (11)	C4—C12—H12C	109.5
C13—N5—C4	119.93 (11)	H12A—C12—H12C	109.5
C6—N5—C4	121.21 (10)	H12B—C12—H12C	109.5
C11—C6—C7	119.78 (12)	O2—C13—N5	124.93 (13)
C11—C6—N5	120.50 (10)	O2—C13—H13	117.5
C7—C6—N5	119.61 (12)	N5—C13—H13	117.5
C11—N1—C2—O1	177.36 (14)	N5—C6—C7—C8	-173.39 (13)
C11—N1—C2—C3	-3.9 (2)	C6—C7—C8—C9	-0.7 (2)
O1—C2—C3—C4	-105.49 (15)	C7—C8—C9—C10	-1.4 (2)
N1—C2—C3—C4	75.77 (15)	C8—C9—C10—C11	1.4 (2)
C2—C3—C4—N5	-52.89 (14)	C7—C6—C11—C10	-2.81 (19)
C2—C3—C4—C12	-176.57 (11)	N5—C6—C11—C10	173.34 (12)
C12—C4—N5—C13	-81.79 (15)	C7—C6—C11—N1	179.59 (12)
C3—C4—N5—C13	153.92 (12)	N5—C6—C11—N1	-4.25 (18)
C12—C4—N5—C6	92.50 (14)	C9—C10—C11—C6	0.7 (2)
C3—C4—N5—C6	-31.80 (15)	C9—C10—C11—N1	178.38 (13)
C13—N5—C6—C11	-118.66 (14)	C2—N1—C11—C6	-42.1 (2)
C4—N5—C6—C11	66.98 (16)	C2—N1—C11—C10	140.35 (15)
C13—N5—C6—C7	57.50 (17)	C6—N5—C13—O2	-176.50 (13)
C4—N5—C6—C7	-116.86 (13)	C4—N5—C13—O2	-2.1 (2)
C11—C6—C7—C8	2.8 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2^i$	0.89 (2)	2.12 (2)	2.9745 (16)	161.3 (18)
$C13-H13\cdots O1^{ii}$	0.93	2.38	3.2220 (18)	150

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+1, y-1/2, -z+1/2$.

Fig. 1

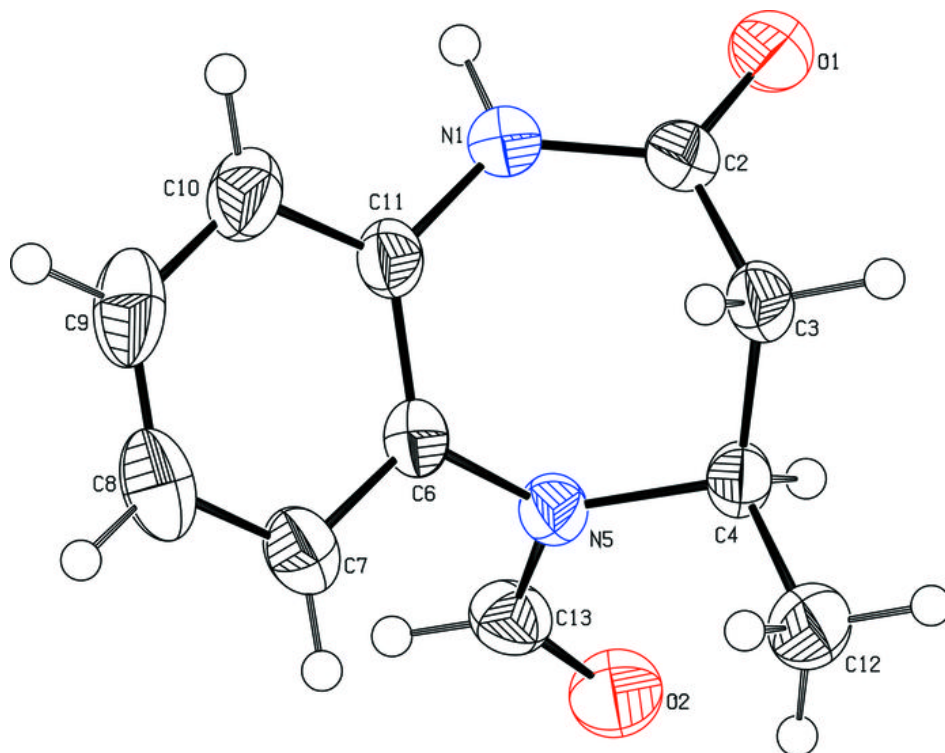


Fig. 2

