



Synthesis, crystal structure and Hirshfeld surface analysis of 3-(4,4-dimethyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-ylidene)-6-methyl-3,4-dihydro-2H-pyran-2,4-dione

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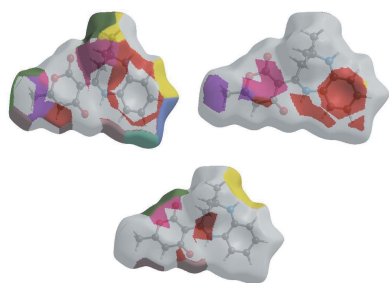
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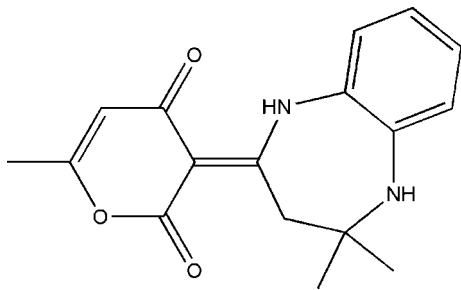
The title compound, C₁₇H₁₈N₂O₃, is constructed from a benzodiazepine ring system linked to a pendant dihydropyran ring, where the benzene and pendant dihydropyran rings are oriented at a dihedral angle of 15.14 (4)°. Intramolecular N—H_{Diazp}···O_{Dhydp} and C—H_{Diazp}···O_{Dhydp} (Diazp = diazepine and Dhydp = dihydropyran) hydrogen bonds link the seven-membered diazepine ring to the pendant dihydropyran ring, enclosing S(6) ring motifs. In the crystal, N—H_{Diazp}···O_{Dhydp} hydrogen bonds link the molecules into infinite chains along [10 $\bar{1}$]. These chains are further linked *via* C—H_{Bnz}···O_{Dhydp}, C—H_{Dhydp}···O_{Dhydp} and C—H_{Mth}···O_{Dhydp} (Bnz = benzene and Mth = methyl) hydrogen bonds, forming a three-dimensional network. The observed weak C—H_{Diazp}··· π interaction may further stabilize the structure. Hirshfeld surface analysis of the crystal structure indicates that the most important contributions for the crystal packing are from H···H (51.1%), H···C/C···H (25.3%) and H···O/O···H (20.3%) interactions. Hydrogen bonding and van der Waals interactions are the dominant interactions in the crystal packing.

1. Chemical context

Derivatives of 1,5-benzodiazepines have attracted considerable attention from researchers because of their bioactive and pharmaceutical properties. Many members of this family are widely used as anticonvulsant, anti-anxiety, anti-seizure, analgesic, sedative, antidepressive and hypnotic or anti-inflammatory agents (Kudo, 1982; Roma *et al.*, 1991; Rajarao *et al.*, 2007; Kumar & Joshi, 2007; Guerrini *et al.*, 2006). Diversely substituted 1,5-benzodiazepines and their derivatives embedded with a variety of functional groups are important biological agents that have been the subject of a significant amount of research activity (Kotyatkina *et al.*, 2001; Fruscella *et al.*, 2001; Zellou *et al.*, 1998*a,b*). Over the last decade, biological interest in 1,5-benzodiazepines has extended to include their use as antibacterial and antifungal agents (Kalkhambkar *et al.*, 2008; Smith *et al.*, 1998). Benzodiazepine derivatives also find commercial use as dyes for acrylic fibers and as intermediates in the synthesis of several heterocyclic systems (Essassi & Salem, 1985; Minnih *et al.*,



2014; Rida *et al.*, 2018). The search for new heterocyclic systems including the 1,5-benzodiazepine moiety for biological activities is therefore of much current importance (Essassi & Salem, 1985; Dardouri *et al.*, 2011; Chkirate *et al.*, 2018; Keita *et al.*, 2003; Jabli *et al.*, 2009). In this context, we synthesized the title compound namely 3-(4,4-dimethyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepin-2-ylidene)-6-methyl-3,4-dihydro-2*H*-pyran-2,4-dione by reacting dehydroacetic acid and *o*-phenylenediamine in ethanol, and we report here the synthesis, the molecular and crystal structures along with the Hirshfeld surface analysis.



2. Structural commentary

The title compound, (I), is built up from a benzodiazepine ring system linked to a pendant dihydropyran ring, (C: O3/C10–C14) (Fig. 1). Ring C is planar within 0.0381 (13) Å (for atom C10), and is oriented at a dihedral angle of 15.14 (4)° with respect to the benzene (B: C4–C9) ring. A puckering analysis of the seven-membered diazepine ring (A: N1/N2/C1–C4/C9) gave the parameters $Q_T = 0.6874$ (14), $q_2 = 0.5903$ (14), $q_3 = 0.3523$ (14) Å, $\varphi_2 = 352.88$ (14), $\varphi_3 = 245.8$ (2)°. In ring A, the N1–C1–C2 [117.10 (2)°], C1–C2–C3 [114.17 (11)°], C3–N2–C4 [128.91 (11)°], N2–C4–C9 [127.38 (12)°], C4–C9–N1 [126.21 (12)°] and C9–N1–C1 [130.71 (12)°] bond angles are enlarged, while the C2–C3–N2 [108.97 (11)°] bond angle is narrowed, when compared with the corresponding values in the seven-membered diazepine ring in the closely related

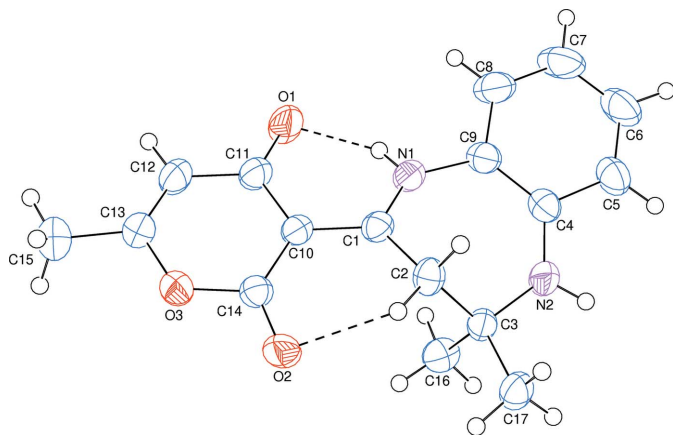


Figure 1

The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. N–H_{Diazp}...O_{Dhydp} and C–H_{Diazp}...O_{Dhydp} (Diazp = diazepine and Dhydp = dihydropyran) hydrogen bonds are shown as dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

C_g is the centroid of the C4–C9 ring.

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1...O1	0.86	1.79	2.5351 (18)	143
N2–H2...O2 ^v	0.86	2.16	2.9990 (16)	166
C2–H2A...O2	0.97	2.12	2.8628 (17)	132
C5–H5...O2 ^v	0.93	2.72	3.453 (2)	136
C12–H12...O1 ⁱ	0.93	2.45	3.3789 (18)	174
C16–H16A...O2 ^{iv}	0.96	2.48	3.3646 (18)	154
C2–H2B...C _g ^{vi}	0.97	2.63	3.4428 (15)	141

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

compound, 3,4-dihydro-2-(2,4-dioxo-6-methylpyran-3-ylidene)-4-(4-pyridin-4-yl)-1,5-benzodiazepine, (II), where the pendant dihydropyran ring is not planar (El Ghayati *et al.*, 2019). On the other hand, the N1–C1 [1.3168 (18) Å], N2–C3 [1.4542 (17) Å], N2–C4 [1.3584 (19) Å], C1–C2 [1.4907 (18) Å] and C2–C3 [1.5444 (18) Å] bond lengths in ring A in (I) may be compared with the corresponding values of N2–C9 [1.3206 (18) Å], N1–C7 [1.4648 (18) Å], N1–C6 [1.3996 (18) Å], C8–C9 [1.5020 (18) Å] and C7–C8 [1.5291 (19) Å] in (II).

In the molecule of (I), N–H_{Diazp}...O_{Dhydp} and C–H_{Diazp}...O_{Dhydp} (Diazp = diazepine and Dhydp = dihydropyran) hydrogen bonds (Table 1) link the seven-membered diazepine ring A to the pendant dihydropyran ring C, enclosing S(6) ring motifs (Fig. 1).

3. Supramolecular features

In the crystal, N–H_{Diazp}...O_{Dhydp} hydrogen bonds (Table 1) link the molecules into infinite chains along [10 $\bar{1}$]. These chains are further linked *via* C–H_{Bnz}...O_{Dhydp}, C–H_{Dhydp}...O_{Dhydp} and C–H_{Mth}...O_{Dhydp} (Bnz = benzene and Mth = methyl) hydrogen bonds (Table 1), forming a three-dimensional network (Fig. 2). The weak C–H_{Diazp}... π interaction (Table 1) may further stabilize the structure.

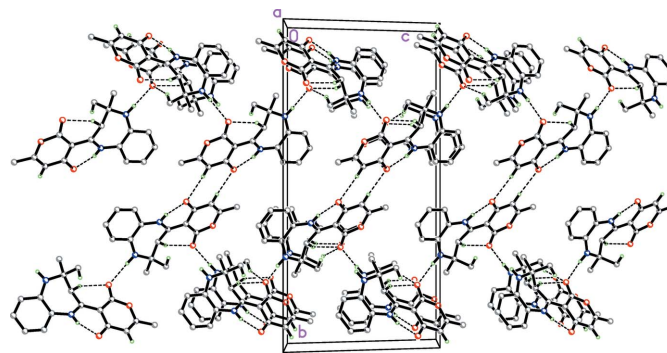


Figure 2

A partial packing diagram viewed along the *a* axis. N–H...O and C–H...O hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted for clarity.

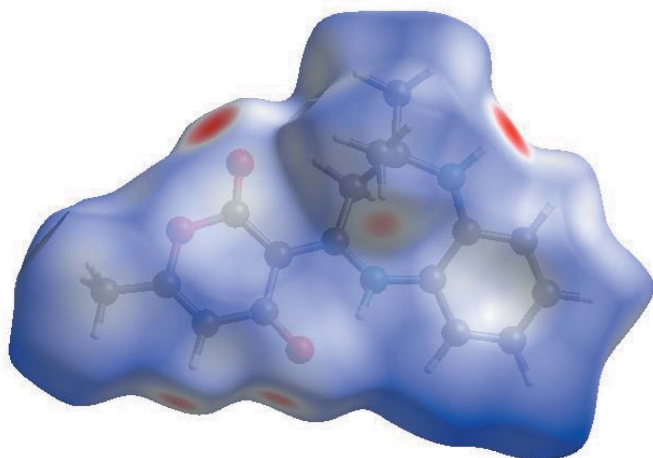


Figure 3
View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range -0.4583 to 1.6329 a.u.

4. Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the crystal of the title compound, a Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out by using *CrystalExplorer17.5* (Turner *et al.*, 2017). In the HS plotted over d_{norm} (Fig. 3), the white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii, respectively (Venkatesan *et al.*, 2016). The bright-red spots appearing near atoms O1 and O2 and hydrogen atoms H2, H12 and H16A indicate their roles as the respective donors and/or acceptors in the dominant $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 1); they also appear as blue and

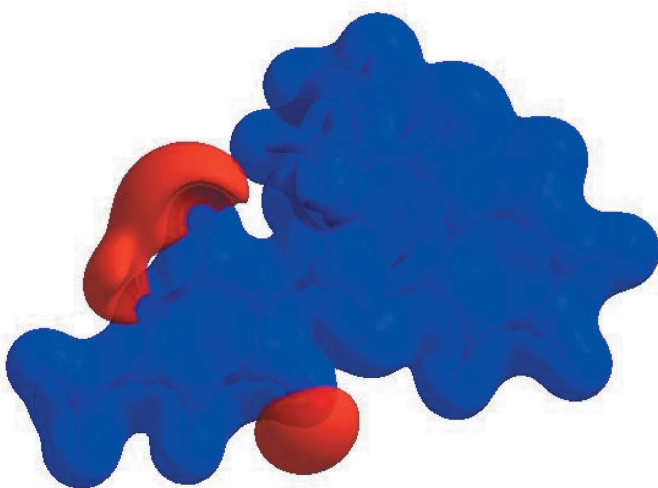


Figure 4
View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential in the range -0.0500 to 0.0500 a.u. using the STO-3 G basis set at the Hartree-Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms, corresponding to positive and negative potentials, respectively.

Table 2
Selected interatomic distances (Å).

O1...N1	2.5351 (18)	C6...H2B ^{iv}	2.95
O1...C12 ⁱ	3.379 (2)	C7...H2B ^{iv}	2.92
O2...N2 ⁱⁱ	2.9990 (16)	C8...H2B ^{iv}	2.94
O2...C2	2.8628 (17)	C9...H2B	2.85
O1...H12 ⁱ	2.45	C11...H1	2.35
O1...H1	1.79	C14...H2A	2.58
O2...H2A	2.12	C14...H17C ⁱⁱⁱ	2.95
O2...H2 ⁱⁱ	2.16	C16...O2 ^{iv}	3.3648 (19)
O2...H5 ⁱⁱ	2.72	H1...H8	2.24
O2...H17C ⁱⁱⁱ	2.91	H2...H5	2.21
N1...N2	3.0698 (17)	H2...H17A	2.27
N1...C16	3.3656 (19)	H2...H17C	2.59
N2...N1	3.0698 (17)	H2A...H17B	2.42
N1...H16A	2.8152	H2B...H17C	2.57
C4...C2 ^{iv}	3.5887 (17)	H5...H16B ^v	2.42
C9...C2 ^{iv}	3.533 (2)	H5...H17B ^v	2.51
C14...C17 ⁱⁱⁱ	3.404 (2)	H12...H15B	2.45
C1...H16A	2.62	H12...H12 ⁱ	2.55
C4...H2B	2.79	H16A...O2 ^{iv}	2.48
C5...H2B ^{iv}	2.99	H16B...H17B	2.52
C5...H16B ^v	2.99	H16C...H17A	2.50

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

red regions corresponding to positive and negative potentials on the HS mapped over electrostatic potential (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) shown in Fig. 4 where the blue regions indicate positive electrostatic potential (hydrogen-bond donors) and the red regions indicate negative electrostatic potential (hydrogen-bond acceptors). The shape-index of the HS is a tool to visualize the $\pi-\pi$ stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no $\pi-\pi$ interactions. Fig. 5 clearly suggest that there are no $\pi-\pi$ interactions in (I).

The overall two-dimensional fingerprint plot, Fig. 6a, and those delineated into $\text{H}\cdots\text{H}$, $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$, $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{O}\cdots\text{O}$ and $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 6b-f, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is $\text{H}\cdots\text{H}$, contributing 51.1% to the overall

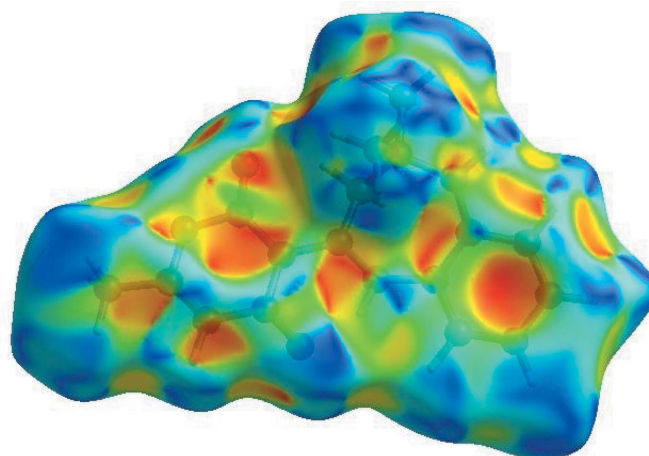
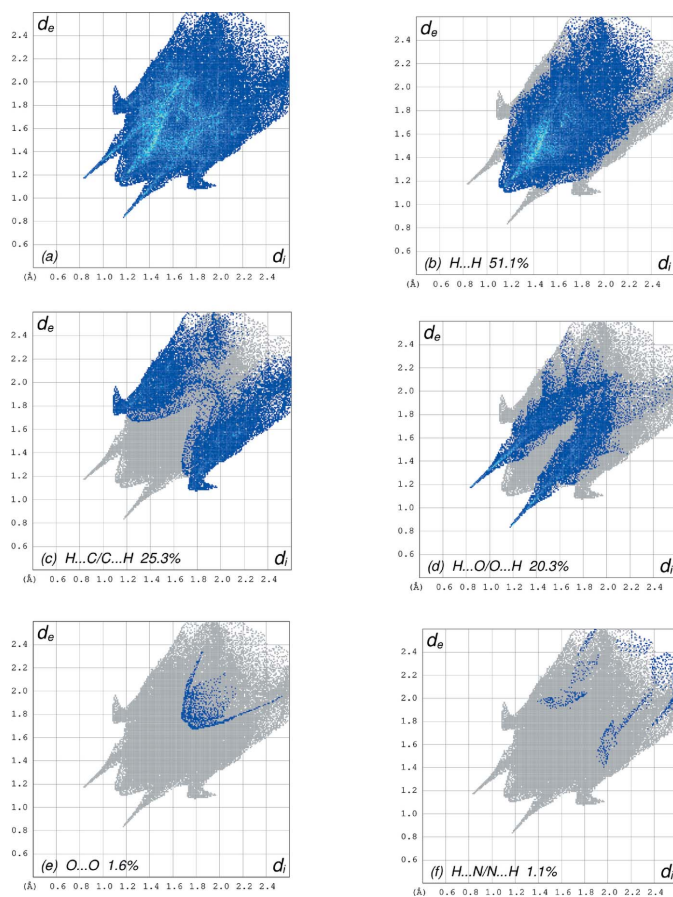


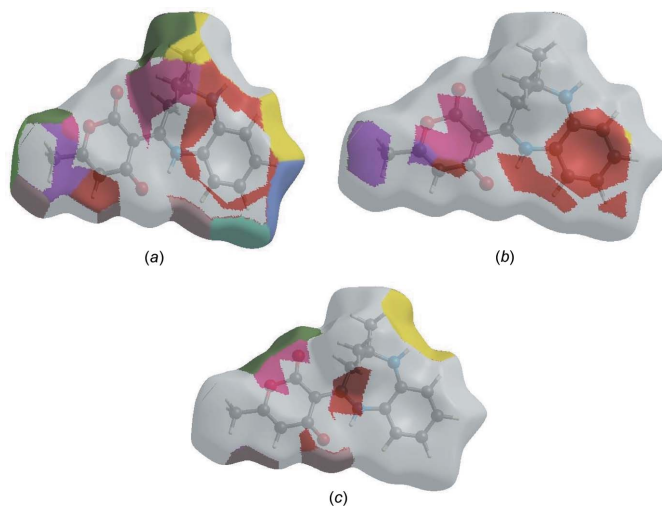
Figure 5
Hirshfeld surface of the title compound plotted over shape-index.


Figure 6

The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) H...H, (c) H...C/C...H, (d) H...O/O...H, (e) O...O and (f) H...N/N...H interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

crystal packing, which is reflected in Fig. 6b as widely scattered points of high density due to the large hydrogen content of the molecule. The spike with the tip at $d_e = d_i = 1.14$ Å in Fig. 6b is due to the short interatomic H...H contacts (Table 2). In the presence of C—H... π interactions, the pair of wings in the fingerprint plot delineated into H...C/C...H contacts with 25.3% contribution to the HS show a nearly symmetrical distribution of points, Fig. 6c, with the thin edges at $d_e + d_i \sim 2.81$ Å arising from the H...C/C...H contacts (Table 2). There is a pair of characteristic wings in the fingerprint plot delineated into H...O/O...H contacts, Fig. 6d: the 20.3% contribution to the HS arises from the N—H...O and C—H...O hydrogen bonds (Table 1) as well as from the H...O/O...H contacts (Table 2) and is shown as a pair of spikes with the tips at $d_e + d_i = 2.00$ Å. Finally, the weak O...O (Fig. 6e) and H...N/N...H (Fig. 6f) contacts in the structure contribute only 1.6 and 1.1%, respectively, to the HS. The Hirshfeld surface representations with the function d_{norm} plotted onto the surface are shown for the H...H, H...C/C...H and H...O/O...H interactions in Fig. 7a–c, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number


Figure 7

The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for (a) H...H, (b) H...C/C...H and (c) H...O/O...H interactions.

of H...H, H...C/C...H and H...O/O...H interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

5. Synthesis and crystallization

A solution of dehydroacetic acid (0.168 g, 1 mmol) and *o*-phenylenediamine (0.108 g, 1 mmol) in ethanol (40 ml) was refluxed for 1 h. After cooling to room temperature, the colourless intermediate solid compound, a mono-Schiff base, was obtained in 70% yield. The intermediate (0.5 g, 1 mmol) was refluxed in acetone (10 ml) for 1 h. After cooling, the crystals formed were filtered and dried (yield: 65%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. N- and C-bound H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, respectively) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{N, C})$, where $k = 1.5$ for methyl H atoms and 1.2 for the other H atoms.

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₇ H ₁₈ N ₂ O ₃
<i>M_r</i>	298.33
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.5373 (1), 24.0197 (4), 11.7815 (3)
β (°)	103.488 (2)
<i>V</i> (Å ³)	1523.77 (6)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	0.74
Crystal size (mm)	0.42 × 0.38 × 0.16
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.700, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	9860, 2934, 2519
<i>R</i> _{int}	0.023
(sin θ/λ) _{max} (Å ⁻¹)	0.614
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.112, 1.05
No. of reflections	2934
No. of parameters	203
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.20, -0.16

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015b), *SHELXL2014* (Sheldrick, 2015a) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Synthesis, crystal structure and Hirshfeld surface analysis of 3-(4,4-dimethyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepin-2-ylidene)-6-methyl-3,4-dihydro-2*H*-pyran-2,4-dione

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015a); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

3-(4,4-Dimethyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepin-2-ylidene)-6-methyl-3,4-dihydro-2*H*-pyran-2,4-dione

Crystal data

$C_{17}H_{18}N_2O_3$

$M_r = 298.33$

Monoclinic, $P2_1/n$

$a = 5.5373$ (1) Å

$b = 24.0197$ (4) Å

$c = 11.7815$ (3) Å

$\beta = 103.488$ (2)°

$V = 1523.77$ (6) Å³

$Z = 4$

$F(000) = 632$

$D_x = 1.300$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 4280 reflections

$\theta = 3.8$ – 71.5 °

$\mu = 0.74$ mm⁻¹

$T = 296$ K

Prism, yellow

$0.42 \times 0.38 \times 0.16$ mm

Data collection

Rigaku Oxford Diffraction
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 16.0416 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Rigaku OD 2015)

$T_{\min} = 0.700$, $T_{\max} = 1.000$

9860 measured reflections

2934 independent reflections

2519 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 71.3$ °, $\theta_{\min} = 3.7$ °

$h = -5 \rightarrow 6$

$k = -27 \rightarrow 29$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.112$

$S = 1.05$

2934 reflections

203 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.3037P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2014 (Sheldrick, 2015a),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0020 (3)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.9607 (2)	0.55040 (5)	0.34659 (11)	0.0620 (4)
O2	0.3736 (2)	0.69299 (4)	0.35380 (9)	0.0499 (3)
O3	0.45601 (19)	0.62933 (4)	0.48899 (9)	0.0430 (3)
N1	0.8514 (2)	0.61406 (5)	0.17042 (11)	0.0406 (3)
H1	0.9435	0.5909	0.2170	0.049*
N2	0.7655 (3)	0.71643 (5)	0.01003 (11)	0.0478 (3)
H2	0.7686	0.7426	-0.0394	0.057*
C1	0.6776 (2)	0.63806 (5)	0.21295 (12)	0.0350 (3)
C2	0.5128 (2)	0.67882 (6)	0.13633 (12)	0.0382 (3)
H2A	0.3856	0.6910	0.1752	0.046*
H2B	0.4303	0.6602	0.0648	0.046*
C3	0.6492 (2)	0.73059 (5)	0.10487 (11)	0.0342 (3)
C4	0.8700 (2)	0.66752 (6)	-0.01123 (12)	0.0377 (3)
C5	0.9507 (3)	0.66471 (7)	-0.11604 (14)	0.0491 (4)
H5	0.9191	0.6948	-0.1670	0.059*
C6	1.0733 (4)	0.61968 (8)	-0.14591 (17)	0.0644 (5)
H6	1.1245	0.6198	-0.2157	0.077*
C7	1.1215 (4)	0.57393 (8)	-0.0726 (2)	0.0733 (6)
H7	1.2073	0.5434	-0.0917	0.088*
C8	1.0400 (4)	0.57462 (7)	0.02874 (18)	0.0597 (5)
H8	1.0711	0.5439	0.0780	0.072*
C9	0.9117 (3)	0.62000 (6)	0.06068 (13)	0.0406 (3)
C10	0.6538 (2)	0.62144 (5)	0.32672 (12)	0.0355 (3)
C11	0.7997 (3)	0.57556 (6)	0.38662 (13)	0.0434 (3)
C12	0.7494 (3)	0.55810 (6)	0.49603 (13)	0.0483 (4)
H12	0.8365	0.5281	0.5357	0.058*
C13	0.5820 (3)	0.58377 (6)	0.54124 (13)	0.0429 (3)
C14	0.4890 (2)	0.65029 (5)	0.38391 (11)	0.0360 (3)
C15	0.5058 (4)	0.56883 (8)	0.65044 (15)	0.0594 (4)
H15A	0.5417	0.5993	0.7045	0.089*
H15B	0.5957	0.5364	0.6845	0.089*
H15C	0.3309	0.5611	0.6327	0.089*
C16	0.8401 (3)	0.75272 (6)	0.20995 (13)	0.0459 (4)

H16A	0.9684	0.7255	0.2348	0.069*
H16B	0.7605	0.7602	0.2725	0.069*
H16C	0.9118	0.7864	0.1888	0.069*
C17	0.4561 (3)	0.77557 (6)	0.05783 (13)	0.0457 (4)
H17A	0.5355	0.8065	0.0297	0.069*
H17B	0.3814	0.7880	0.1192	0.069*
H17C	0.3303	0.7605	-0.0049	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0764 (8)	0.0527 (7)	0.0685 (8)	0.0335 (6)	0.0406 (6)	0.0244 (6)
O2	0.0595 (7)	0.0469 (6)	0.0441 (6)	0.0227 (5)	0.0136 (5)	0.0028 (4)
O3	0.0484 (6)	0.0432 (5)	0.0407 (5)	0.0071 (4)	0.0171 (4)	0.0020 (4)
N1	0.0468 (7)	0.0331 (6)	0.0463 (7)	0.0048 (5)	0.0197 (5)	0.0062 (5)
N2	0.0655 (8)	0.0409 (6)	0.0456 (7)	0.0080 (6)	0.0304 (6)	0.0104 (5)
C1	0.0371 (7)	0.0296 (6)	0.0400 (7)	-0.0031 (5)	0.0122 (5)	0.0007 (5)
C2	0.0335 (6)	0.0443 (7)	0.0373 (7)	-0.0013 (5)	0.0095 (5)	0.0056 (6)
C3	0.0351 (7)	0.0353 (7)	0.0338 (6)	0.0037 (5)	0.0110 (5)	0.0048 (5)
C4	0.0371 (7)	0.0405 (7)	0.0375 (7)	-0.0075 (5)	0.0131 (5)	-0.0052 (5)
C5	0.0563 (9)	0.0541 (9)	0.0424 (8)	-0.0096 (7)	0.0225 (7)	-0.0055 (6)
C6	0.0835 (13)	0.0615 (10)	0.0630 (11)	-0.0134 (9)	0.0472 (10)	-0.0181 (9)
C7	0.0968 (15)	0.0455 (9)	0.0989 (15)	-0.0026 (9)	0.0660 (13)	-0.0179 (9)
C8	0.0756 (12)	0.0344 (7)	0.0830 (12)	-0.0005 (7)	0.0469 (10)	-0.0019 (7)
C9	0.0441 (7)	0.0350 (7)	0.0486 (8)	-0.0060 (5)	0.0223 (6)	-0.0053 (6)
C10	0.0395 (7)	0.0297 (6)	0.0389 (7)	0.0018 (5)	0.0125 (6)	0.0026 (5)
C11	0.0495 (8)	0.0355 (7)	0.0492 (8)	0.0087 (6)	0.0197 (6)	0.0079 (6)
C12	0.0584 (9)	0.0408 (7)	0.0483 (8)	0.0116 (6)	0.0178 (7)	0.0142 (6)
C13	0.0509 (8)	0.0389 (7)	0.0398 (7)	-0.0001 (6)	0.0128 (6)	0.0038 (6)
C14	0.0378 (7)	0.0342 (6)	0.0351 (6)	0.0023 (5)	0.0067 (5)	-0.0004 (5)
C15	0.0751 (11)	0.0606 (10)	0.0477 (9)	0.0014 (8)	0.0251 (8)	0.0077 (7)
C16	0.0445 (8)	0.0412 (8)	0.0490 (8)	0.0001 (6)	0.0048 (6)	-0.0002 (6)
C17	0.0462 (8)	0.0482 (8)	0.0437 (8)	0.0121 (6)	0.0127 (6)	0.0121 (6)

Geometric parameters (Å, °)

O1—C11	1.2569 (18)	C6—H6	0.9300
O2—C14	1.2167 (17)	C6—C7	1.385 (3)
O3—C13	1.3649 (18)	C7—H7	0.9300
O3—C14	1.3874 (16)	C7—C8	1.372 (3)
N1—H1	0.8600	C8—H8	0.9300
N1—C1	1.3168 (18)	C8—C9	1.400 (2)
N1—C9	1.4158 (18)	C10—C11	1.4487 (18)
N2—H2	0.8600	C10—C14	1.4331 (18)
N2—C3	1.4542 (17)	C11—C12	1.443 (2)
N2—C4	1.3584 (19)	C12—H12	0.9300
C1—C2	1.4907 (18)	C12—C13	1.324 (2)
C1—C10	1.4338 (18)	C13—C15	1.488 (2)

C2—H2A	0.9700	C15—H15A	0.9600
C2—H2B	0.9700	C15—H15B	0.9600
C2—C3	1.5444 (18)	C15—H15C	0.9600
C3—C16	1.524 (2)	C16—H16A	0.9600
C3—C17	1.5301 (18)	C16—H16B	0.9600
C4—C5	1.4094 (19)	C16—H16C	0.9600
C4—C9	1.408 (2)	C17—H17A	0.9600
C5—H5	0.9300	C17—H17B	0.9600
C5—C6	1.366 (2)	C17—H17C	0.9600
O1…N1	2.5351 (18)	C6…H2B ^{iv}	2.95
O1…C12 ⁱ	3.379 (2)	C7…H2B ^{iv}	2.92
O2…N2 ⁱⁱ	2.9990 (16)	C8…H2B ^{iv}	2.94
O2…C2	2.8628 (17)	C9…H2B	2.85
O1…H12 ⁱ	2.45	C11…H1	2.35
O1…H1	1.79	C14…H2A	2.58
O2…H2A	2.12	C14…H17C ⁱⁱⁱ	2.95
O2…H2 ⁱⁱ	2.16	C16…O2 ^{iv}	3.3648 (19)
O2…H5 ⁱⁱ	2.72	H1…H8	2.24
O2…H17C ⁱⁱⁱ	2.91	H2…H5	2.21
N1…N2	3.0698 (17)	H2…H17A	2.27
N1…C16	3.3656 (19)	H2…H17C	2.59
N2…N1	3.0698 (17)	H2A…H17B	2.42
N1…H16A	2.8152	H2B…H17C	2.57
C4…C2 ^{iv}	3.5887 (17)	H5…H16B ^v	2.42
C9…C2 ^{iv}	3.533 (2)	H5…H17B ^v	2.51
C14…C17 ⁱⁱⁱ	3.404 (2)	H12…H15B	2.45
C1…H16A	2.62	H12…H12 ⁱ	2.55
C4…H2B	2.79	H16A…O2 ^{iv}	2.48
C5…H2B ^{iv}	2.99	H16B…H17B	2.52
C5…H16B ^v	2.99	H16C…H17A	2.50
C13—O3—C14	122.24 (11)	C4—C9—N1	126.21 (12)
C1—N1—H1	114.6	C8—C9—N1	114.18 (14)
C1—N1—C9	130.71 (12)	C8—C9—C4	119.45 (14)
C9—N1—H1	114.6	C1—C10—C11	120.32 (12)
C3—N2—H2	115.5	C14—C10—C1	120.82 (12)
C4—N2—H2	115.5	C14—C10—C11	118.85 (12)
C4—N2—C3	128.91 (11)	O1—C11—C10	123.15 (13)
N1—C1—C2	117.10 (12)	O1—C11—C12	119.80 (13)
N1—C1—C10	117.94 (12)	C12—C11—C10	117.03 (12)
C10—C1—C2	124.90 (12)	C11—C12—H12	119.2
C1—C2—H2A	108.7	C13—C12—C11	121.53 (13)
C1—C2—H2B	108.7	C13—C12—H12	119.2
C1—C2—C3	114.17 (11)	O3—C13—C15	111.40 (13)
H2A—C2—H2B	107.6	C12—C13—O3	121.61 (13)
C3—C2—H2A	108.7	C12—C13—C15	126.99 (14)
C3—C2—H2B	108.7	O2—C14—O3	113.36 (12)

N2—C3—C2	108.97 (11)	O2—C14—C10	128.26 (13)
N2—C3—C16	110.99 (12)	O3—C14—C10	118.35 (11)
N2—C3—C17	106.51 (11)	C13—C15—H15A	109.5
C16—C3—C2	111.80 (11)	C13—C15—H15B	109.5
C16—C3—C17	109.98 (12)	C13—C15—H15C	109.5
C17—C3—C2	108.41 (11)	H15A—C15—H15B	109.5
N2—C4—C5	116.02 (13)	H15A—C15—H15C	109.5
N2—C4—C9	127.38 (12)	H15B—C15—H15C	109.5
C9—C4—C5	116.58 (13)	C3—C16—H16A	109.5
C4—C5—H5	118.6	C3—C16—H16B	109.5
C6—C5—C4	122.80 (16)	C3—C16—H16C	109.5
C6—C5—H5	118.6	H16A—C16—H16B	109.5
C5—C6—H6	119.9	H16A—C16—H16C	109.5
C5—C6—C7	120.20 (15)	H16B—C16—H16C	109.5
C7—C6—H6	119.9	C3—C17—H17A	109.5
C6—C7—H7	120.7	C3—C17—H17B	109.5
C8—C7—C6	118.58 (16)	C3—C17—H17C	109.5
C8—C7—H7	120.7	H17A—C17—H17B	109.5
C7—C8—H8	118.9	H17A—C17—H17C	109.5
C7—C8—C9	122.30 (17)	H17B—C17—H17C	109.5
C9—C8—H8	118.9		
C9—N1—C1—C10	177.02 (13)	C1—N1—C9—C8	-157.26 (15)
C9—N1—C1—C2	-0.3 (2)	C1—N1—C9—C4	27.4 (2)
N1—C1—C2—C3	-63.12 (16)	N1—C1—C10—C14	172.65 (12)
C10—C1—C2—C3	119.73 (14)	C2—C1—C10—C14	-10.2 (2)
C4—N2—C3—C16	88.57 (18)	N1—C1—C10—C11	-6.4 (2)
C4—N2—C3—C17	-151.73 (15)	C2—C1—C10—C11	170.76 (13)
C4—N2—C3—C2	-35.0 (2)	C14—C10—C11—O1	-175.06 (15)
C1—C2—C3—N2	80.67 (14)	C1—C10—C11—O1	4.0 (2)
C1—C2—C3—C16	-42.38 (16)	C14—C10—C11—C12	6.4 (2)
C1—C2—C3—C17	-163.79 (12)	C1—C10—C11—C12	-174.60 (13)
C3—N2—C4—C9	-6.6 (3)	O1—C11—C12—C13	179.64 (16)
C3—N2—C4—C5	174.97 (14)	C10—C11—C12—C13	-1.7 (2)
N2—C4—C5—C6	175.76 (16)	C11—C12—C13—O3	-2.6 (3)
C9—C4—C5—C6	-2.8 (2)	C11—C12—C13—C15	177.58 (16)
C4—C5—C6—C7	0.6 (3)	C14—O3—C13—C12	2.2 (2)
C5—C6—C7—C8	1.1 (3)	C14—O3—C13—C15	-177.94 (13)
C6—C7—C8—C9	-0.4 (3)	C13—O3—C14—O2	-175.69 (13)
C7—C8—C9—C4	-1.9 (3)	C13—O3—C14—C10	2.60 (19)
C7—C8—C9—N1	-177.57 (18)	C1—C10—C14—O2	-7.8 (2)
N2—C4—C9—C8	-174.98 (16)	C11—C10—C14—O2	171.19 (14)
C5—C4—C9—C8	3.4 (2)	C1—C10—C14—O3	174.15 (12)
N2—C4—C9—N1	0.1 (2)	C11—C10—C14—O3	-6.81 (19)
C5—C4—C9—N1	178.49 (14)		

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1/2, -y+3/2, z+1/2$; (iii) $x+1/2, -y+3/2, z+1/2$; (iv) $x+1, y, z$; (v) $x+1/2, -y+3/2, z-1/2$.

Hydrogen-bond geometry (Å, °)

Cg is the centroid of the C4–C9 ring.

<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>
N1—H1···O1	0.86	1.79	2.5351 (18)	143
N2—H2···O2 ^v	0.86	2.16	2.9990 (16)	166
C2—H2 <i>A</i> ···O2	0.97	2.12	2.8628 (17)	132
C5—H5···O2 ^v	0.93	2.72	3.453 (2)	136
C12—H12···O1 ⁱ	0.93	2.45	3.3789 (18)	174
C16—H16 <i>A</i> ···O2 ^{iv}	0.96	2.48	3.3646 (18)	154
C2—H2 <i>B</i> ···Cg ^{vi}	0.97	2.63	3.4428 (15)	141

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (iv) $x+1, y, z$; (v) $x+1/2, -y+3/2, z-1/2$; (vi) $x-1, y, z$.