research communications

Syntheses and crystal structures of two piperine derivatives

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The title compounds, 5-(2H-1,3-benzodioxol-5-yl)-N-cyclohexylpenta-2,4-diena-mide, $C_{18}H_{21}NO_3$ (I), and 5-(2H-1,3-benzodioxol-5-yl)-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one $C_{16}H_{17}NO_3$ (II), are derivatives of piperine, which is known as a pungent component of pepper. Their geometrical parameters are similar to those of the three polymorphs of piperine, which indicate conjugation of electrons over the length of the molecules. The extended structure of (I) features N—H···O amide hydrogen bonds, which generate $C(4)$ [010] chains. The crystal of (II) features aromatic π–π stacking, as for two of three known piperine polymorphs.

1. Chemical context

Piperine [(2E,4E)-1-[5-(1,3-benzodioxol-5yl)-1-oxo-2,4-pentadienyl]piperidine, $C_{17}H_{19}NO_3$, is the major pungent ingredient of Piperaceae pepper (*Piper nigrum*). Piperine is an amide having a methylenedioxyphenyl grouping as a characteristic of its chemical structure (Fig. 1). Interestingly, when the amide group is in a near planar conformation, the conjugated state of the pentadiene chain of piperine has the property that electrons are easily donated and the stretching vibration of the amide carbonyl group is affected (Pfund *et al.*, 2015). As part of our studies in this area, we have already reported a complex using the poorly water-soluble piperine (log P = 2.25) and the cyclic polysaccharide cyclodextrin (Szejtli, 1998; Ezawa *et al.*, 2016). In addition, piperine has been evaluated for its inclusion mechanism and dissolution properties using various cyclodextrins (Ezawa *et al.*, 2018, 2019). The synthesis of piperine derivatives was necessary to understand the inclusion mechanism of piperine and cyclodextrin and the detailed molecular behaviour of piperine.
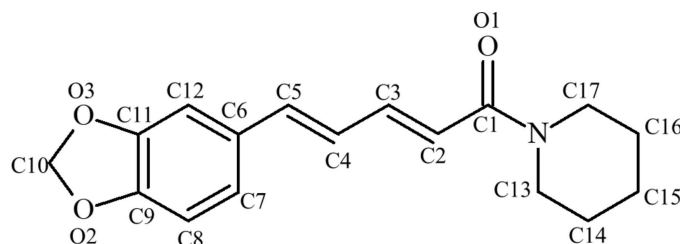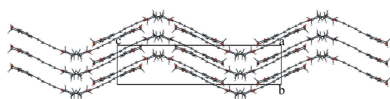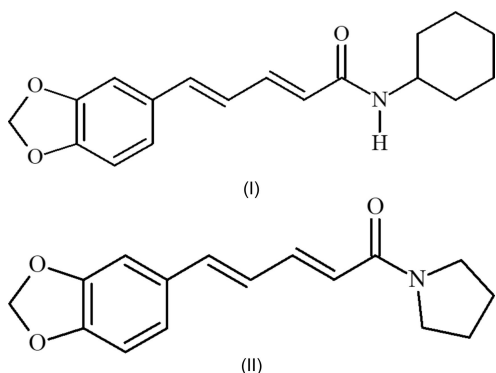
Figure 1
The chemical structure of piperine.

(I)

(II)

Therefore, the aim of this study was to synthesize the title compounds (2*E*,4*E*)-5-(2*H*-1,3-benzodioxol-5-yl)-*N*-cyclohexylpenta-2,4-dienamide, $C_{18}H_{21}NO_3$, (I), and (2*E*,4*E*)-5-(2*H*-1,3-benzodioxol-5-yl)-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one, $C_{16}H_{17}NO_3$, (II), from piperine and to determine their X-ray crystal structures. The log *P* of (I) is 3.36 and that of (II) is 2.36. Assessing the structural properties of the title compounds (crystal structure, geometry, intermolecular interactions, *etc.*) will help to evaluate the inclusion behaviour of piperine with cyclodextrin.

2. Structural commentary

Compound (I) (Fig. 2) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The C1–C6 cyclohexyl ring adopts a chair conformation with the exocyclic C5—N1 bond in an equatorial orientation. The C7–C12/O2/O3 fused-ring system is almost planar (r.m.s. deviation = 0.020 Å) and subtends a dihedral angle of 21.57 (4)° with the cyclohexyl ring. The bond distances and angles (amide, pentadiene and methylenedioxyphenyl moieties) of (I) are not significantly different from the equivalent data for the three polymorphs of piperine (Pfund *et al.*, 2015) (Table 1).
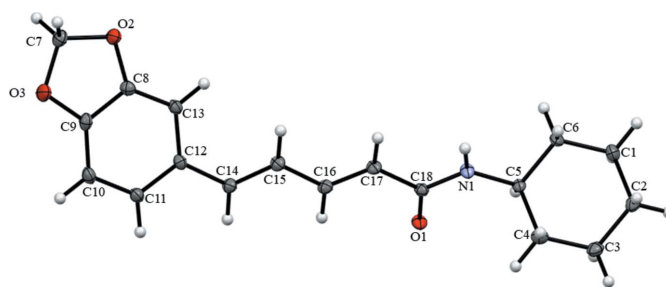

Figure 2
Displacement ellipsoid drawing at a 50% probability level of the asymmetric unit of (I).
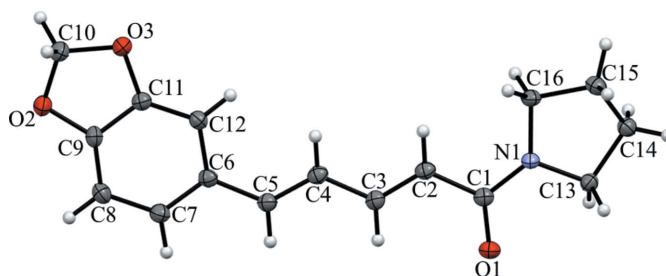

Figure 3
Displacement ellipsoid drawing at a 50% probability level of the asymmetric unit of (II).

Compound (II) (Fig. 3), also known as piperilyn, crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell. The C13–C16/N1 ring is well described as being twisted with C14 and C15 deviating from C13/N1/C16 by 0.205 (2) and −0.382 (2) Å, respectively. The C9/O2/C10/O3/C11 ring has a clear tendency towards an envelope conformation [deviation of C10 from the other four atoms = −0.216 (2) Å]. The dihedral angle between the C13–C16/N1 and C6–C12/O2/O3 rings (all atoms) is 12.29 (10)°. As with (I), the key bond-distance data for (II) are comparable to those of piperine (Table 1).

Thus, we may conclude that the title compounds show intramolecular resonance from the amide group to the ether O

Table 1
Key geometrical parameters (Å) for the title compounds and piperine polymorphs.

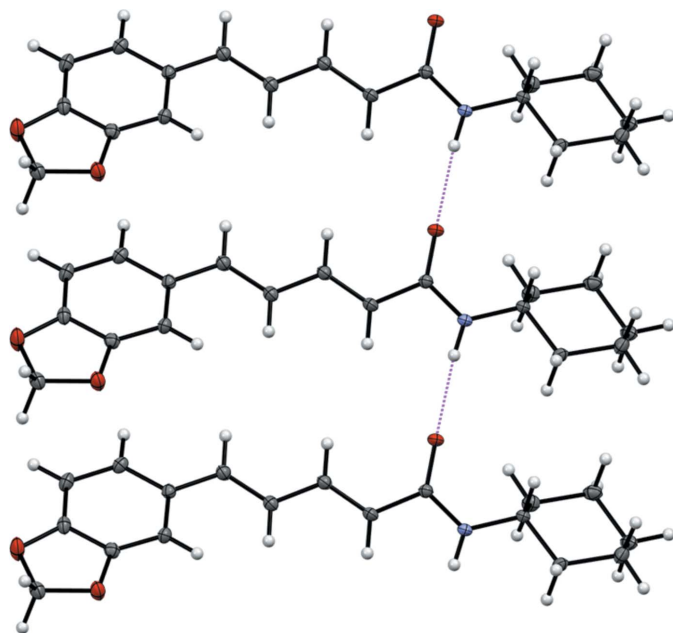|	(I)	(II)	PIPINE10	PIPINE12	PIPINE13
Amide	C18—N1 (1.344)	C1—N1 (1.350)	C1—N1 (1.331)	C1—N1 (1.363)	C1—N1 (1.353)
	C18—O1 (1.242)	C1—O1 (1.243)	C1—O1 (1.218)	C1—O1 (1.235)	C1—O1 (1.482)
Pentadiene	C14—C15 (1.346)	C4—C5 (1.345)	C4—C5 (1.312)	C4—C5 (1.330)	C4—C5 (1.347)
	C15—C16 (1.444)	C3—C4 (1.441)	C3—C4 (1.437)	C3—C4 (1.440)	C3—C4 (1.442)
	C16—C17 (1.342)	C2—C3 (1.332)	C2—C3 (1.311)	C2—C3 (1.332)	C2—C3 (1.341)
	C17—C18 (1.479)	C1—C2 (1.480)	C1—C2 (1.473)	C1—C2 (1.477)	C1—C2 (1.482)
	C8—C9 (1.390)	C6—C7 (1.397)	C6—C7 (1.387)	C6—C7 (1.399)	C6—C7 (1.403)
	C8—C13 (1.371)	C6—C12 (1.412)	C6—C12 (1.396)	C6—C12 (1.414)	C6—C12 (1.412)
	C9—C10 (1.374)	C7—C8 (1.403)	C7—C8 (1.393)	C7—C8 (1.395)	C7—C8 (1.393)
Methylenedioxyphenyl	C10—C11 (1.402)	C8—C9 (1.369)	C8—C9 (1.343)	C8—C9 (1.360)	C8—C9 (1.371)
	C11—C12 (1.399)	C9—C11 (1.385)	C9—C11 (1.357)	C9—C11 (1.377)	C9—C11 (1.381)
	C12—C13 (1.412)	C11—C13 (1.364)	C11—C13 (1.364)	C11—C12 (1.370)	C11—C12 (1.367)
	C8—O2 (1.371)	C9—O2 (1.378)	C9—O2 (1.373)	c9—O2 (1.383)	C9—O2 (1.378)
	C9—O3 (1.370)	C11—O3 (1.376)	C11—O3 (1.362)	C11—O3 (1.383)	C11—O3 (1.383)
π-stacking close contacts		C9···C9 (3.268)		C8···C8 (3.110)	C9···C12 (3.327)
		C9···C12 (3.322)		C8···C8 (3.303)	
		C11···C12 (3.287)			

Figure 4
A view along the *c*-axis direction of the crystal packing of (I). The N—H···O hydrogen bonds are drawn as dashed lines.
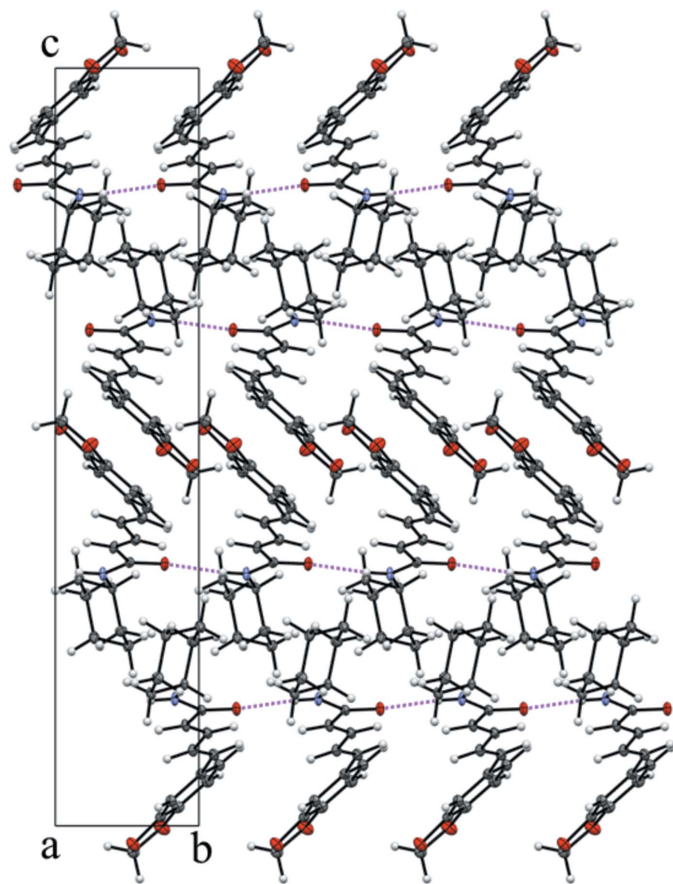

Figure 5
The unit-cell packing for (I) viewed down [100] with hydrogen bonds drawn as dashed lines.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.874 (16)	2.086 (16)	2.9547 (12)	172.8 (14)

Symmetry code: (i) $x, y + 1, z$.

atoms of the methylenedioxyphenyl moiety, similar to piperine.

3. Supramolecular features

Piperine crystallizes in three polymorphs: form I [CCDC (Groom *et al.*, 2016) refcode: PIPINE10] and form II (PIPINE12) in space group $P2_1/n$ and form III (PIPINE13) in space group $C2/c$ (Table 1) (Pfund *et al.*, 2015). The packing for forms II and III features aromatic π–π stacking interactions, while that of form I does not.

The crystal structure of (I) does not feature π–π stacking interactions, which is similar to piperine form I. Compound (I) possesses an N—H grouping, which forms a classical N1—H···O1 hydrogen bond (Table 2) between the amide-bond sites, generating [010] $C(4)$ chains (Fig. 4) with adjacent molecules related by simple translation. The unit-cell packing for (I) is illustrated in Fig. 5.

The structure of (II) does feature π–π stacking with the closest intermolecular contacts being C9···C9 = 3.268 (3), C9···C12 = 3.322 (3) and C11···C12 = 3.287 (3) Å (Fig. 6). The overall packing for (II) can be described as undulating sheets propagating in the (010) plane (Fig. 7).

4. Synthesis and crystallization

Piperine was purchased from Fujifilm Wako Pure Chemical Co., Ltd. The synthesis of piperine derivatives was performed using a previously reported procedure (Takao *et al.*, 2015). After dissolving piperine in ethanol, hydrolysis was performed by stirring for 20 h in the presence of KOH. After evaporating the solvent under vacuum, the resulting reaction mixture was suspended in water and acidified with 4 *M* HCl to pH < 1. The resultant pale-brown precipitate was collected by filtration, washed with cold water and recrystallized from methanol
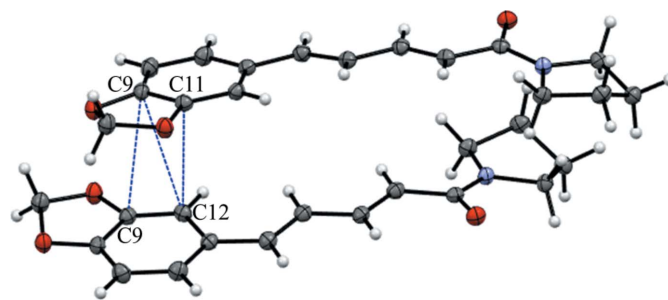

Figure 6
Fragment of the crystal of (II) showing close C···C contacts due to π–π stacking.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{18}H_{21}NO_3$	$C_{16}H_{17}NO_3$
M_r	299.36	271.30
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$
Temperature (K)	90	90
a, b, c (Å)	11.4982 (7), 5.0086 (3), 26.7240 (16)	11.8747 (10), 7.2485 (6), 30.392 (2)
α, β, γ (°)	90, 97.683 (2), 90	90, 90, 90
V (Å^3)	1525.22 (16)	2616.0 (4)
Z	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.10
Crystal size (mm)	$0.58 \times 0.07 \times 0.07$	$0.28 \times 0.06 \times 0.06$
Data collection		
Diffractometer	Bruker D8 goniometer	Bruker D8 goniometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2018)	Multi-scan (*SADABS*; Bruker, 2018)
T_{min}, T_{max}	0.580, 0.747	0.666, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27741, 4862, 4204	41504, 3506, 2193
R_{int}	0.066	0.128
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.725	0.685
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.121, 1.07	0.050, 0.143, 1.05
No. of reflections	4862	3506
No. of parameters	202	182
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.42, −0.26	0.28, −0.26

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *ShelXle* (Hübschle *et al.*, 2011).

solution to give piperic acid. The piperic acid (1.0 mmol) was dissolved in CH_2Cl_2 (5 ml) and oxalyl chloride (10 mmol) was added and the mixture was stirred at room temperature for 3 h. The solvent and excess oxalyl chloride were then evaporated under reduced pressure.

To prepare (I), the crude acid chloride generated was dissolved in CH_2Cl_2 (2 ml) and cyclohexylamine (1.2 mmol) and Et_3N (8 mmol) were added, and the mixture was stirred at 273 K for 5 h. Ice-cold water was added to the mixture, followed by extraction with chloroform (5 ml). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (eluent hexane:etyl acetate 1:1 *v/v*) to give (I) in the form of a yellow powder. Light-yellow needles of (I) were recrystallized from ethyl acetate solution.

Compound (II) was prepared by the same procedure with pyrrolidine (1.2 mmol) replacing the cyclohexylamine to give (II) in the form of a white powder. Colourless needles of (II) were recrystallized from ethyl acetate solution.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms for carbon atom were included in their calculated positions and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydrogen atom attached to N1 in (I) was located in a difference-Fourier map and its position freely refined with $U_{iso}(H) = 1.2U_{eq}(N)$.

Figure 7
The unit-cell packing for (II) viewed down [100].

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Computing details

For both structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ShelXle* (Hübschle *et al.*, 2011); software used to prepare material for publication: *Generate Report* (Bruker, 2018).

5-(2*H*-1,3-Benzodioxol-5-yl)-*N*-cyclohexylpenta-2,4-dienamide (I)

Crystal data

$C_{18}H_{21}NO_3$	$F(000) = 640$
$M_r = 299.36$	$D_x = 1.304$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.4982$ (7) Å	Cell parameters from 9948 reflections
$b = 5.0086$ (3) Å	$\theta = 2.5–33.5°$
$c = 26.7240$ (16) Å	$\mu = 0.09$ mm^{-1}
$\beta = 97.683$ (2)°	$T = 90$ K
$V = 1525.22$ (16) Å^3	Needle, light-yellow
$Z = 4$	$0.58 \times 0.07 \times 0.07$ mm

Data collection

Bruker D8 goniometer diffractometer	27741 measured reflections
Radiation source: microfocus X-ray tube	4862 independent reflections
Multilayered conforacal mirror monochromator	4204 reflections with $I > 2\sigma(I)$
Detector resolution: 7.391 pixels mm^{-1}	$R_{int} = 0.066$
ω scans	$\theta_{max} = 31.0°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2018)	$h = -16 \rightarrow 16$
	$k = -7 \rightarrow 7$
	$l = -38 \rightarrow 38$
$T_{min} = 0.580$, $T_{max} = 0.747$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	
$wR(F^2) = 0.121$	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.7464P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
4862 reflections	$(\Delta/\sigma)_{max} = 0.001$
202 parameters	$\Delta\rho_{max} = 0.42$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}
Primary atom site location: dual	

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.96864 (7)	0.23821 (16)	0.65434 (3)	0.01577 (17)
O2	0.26072 (7)	0.95788 (18)	0.47532 (3)	0.01982 (18)
O3	0.09239 (7)	0.7586 (2)	0.49784 (4)	0.0246 (2)
N1	1.02983 (8)	0.66732 (19)	0.66764 (4)	0.01464 (18)
H1	1.0072 (13)	0.834 (3)	0.6656 (6)	0.018*
C1	1.35763 (10)	0.7868 (2)	0.69502 (4)	0.0179 (2)
H1A	1.387593	0.633931	0.677037	0.021*
H1AB	1.404140	0.946479	0.688562	0.021*
C2	1.37316 (10)	0.7289 (2)	0.75164 (4)	0.0177 (2)
H2A	1.456652	0.689410	0.763536	0.021*
H2AB	1.350298	0.887869	0.770054	0.021*
C3	1.29754 (11)	0.4914 (2)	0.76259 (4)	0.0184 (2)
H3A	1.306633	0.458942	0.799445	0.022*
H3AB	1.324548	0.329830	0.746168	0.022*
C4	1.16802 (10)	0.5412 (2)	0.74321 (4)	0.0174 (2)
H4A	1.121475	0.381401	0.749567	0.021*
H4AB	1.139004	0.693282	0.761708	0.021*
C5	1.15165 (9)	0.6024 (2)	0.68667 (4)	0.01204 (19)
H5	1.174757	0.440743	0.668389	0.014*
C6	1.22876 (10)	0.8346 (2)	0.67461 (4)	0.0156 (2)
H6A	1.201602	1.000303	0.689604	0.019*
H6AB	1.220984	0.859459	0.637563	0.019*
C7	0.13448 (10)	0.9561 (2)	0.46564 (4)	0.0178 (2)
H00F	0.103160	1.134167	0.472821	0.021*
H00G	0.108313	0.912274	0.429779	0.021*
C8	0.29070 (10)	0.7663 (2)	0.51139 (4)	0.0146 (2)
C9	0.19016 (9)	0.6451 (2)	0.52444 (4)	0.0157 (2)
C10	0.19552 (10)	0.4395 (2)	0.55871 (4)	0.0172 (2)
H10	0.126694	0.356487	0.567425	0.021*
C11	0.30804 (10)	0.3586 (2)	0.58014 (4)	0.0154 (2)
H11	0.315407	0.213891	0.603318	0.018*
C12	0.40980 (9)	0.4841 (2)	0.56850 (4)	0.0135 (2)
C13	0.40115 (9)	0.6936 (2)	0.53284 (4)	0.0142 (2)
H13	0.469038	0.780458	0.524074	0.017*
C14	0.52399 (9)	0.3949 (2)	0.59388 (4)	0.0151 (2)
H14	0.528504	0.219194	0.607404	0.018*
C15	0.62312 (9)	0.5413 (2)	0.59963 (4)	0.0153 (2)
H15	0.618873	0.720765	0.588024	0.018*
C16	0.73553 (9)	0.4407 (2)	0.62246 (4)	0.0144 (2)

H16	0.741526	0.256496	0.630909	0.017*
C17	0.83199 (9)	0.5927 (2)	0.63240 (4)	0.0147 (2)
H17	0.825437	0.779183	0.626212	0.018*
C18	0.94810 (9)	0.4819 (2)	0.65259 (4)	0.01252 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0151 (4)	0.0087 (3)	0.0230 (4)	0.0010 (3)	0.0008 (3)	0.0012 (3)
O2	0.0130 (4)	0.0226 (4)	0.0237 (4)	0.0022 (3)	0.0019 (3)	0.0074 (3)
O3	0.0116 (4)	0.0333 (5)	0.0284 (5)	0.0015 (4)	0.0014 (3)	0.0109 (4)
N1	0.0124 (4)	0.0082 (4)	0.0228 (5)	0.0014 (3)	0.0006 (3)	0.0001 (3)
C1	0.0146 (5)	0.0186 (5)	0.0199 (5)	−0.0044 (4)	0.0007 (4)	0.0004 (4)
C2	0.0181 (5)	0.0134 (5)	0.0201 (5)	0.0006 (4)	−0.0034 (4)	−0.0003 (4)
C3	0.0222 (5)	0.0137 (5)	0.0181 (5)	0.0006 (4)	−0.0016 (4)	0.0024 (4)
C4	0.0191 (5)	0.0176 (5)	0.0160 (5)	−0.0002 (4)	0.0037 (4)	0.0016 (4)
C5	0.0112 (4)	0.0089 (4)	0.0158 (5)	0.0010 (3)	0.0012 (3)	0.0004 (3)
C6	0.0160 (5)	0.0119 (5)	0.0181 (5)	−0.0033 (4)	−0.0007 (4)	0.0031 (4)
C7	0.0140 (5)	0.0196 (5)	0.0195 (5)	0.0029 (4)	0.0010 (4)	0.0003 (4)
C8	0.0149 (5)	0.0148 (5)	0.0144 (5)	0.0007 (4)	0.0035 (4)	−0.0001 (4)
C9	0.0106 (4)	0.0198 (5)	0.0167 (5)	0.0007 (4)	0.0020 (4)	−0.0022 (4)
C10	0.0128 (5)	0.0208 (5)	0.0183 (5)	−0.0038 (4)	0.0035 (4)	−0.0010 (4)
C11	0.0148 (5)	0.0160 (5)	0.0156 (5)	−0.0028 (4)	0.0031 (4)	0.0003 (4)
C12	0.0121 (4)	0.0134 (5)	0.0153 (5)	−0.0005 (4)	0.0030 (3)	−0.0015 (4)
C13	0.0117 (4)	0.0145 (5)	0.0169 (5)	−0.0008 (4)	0.0037 (4)	0.0006 (4)
C14	0.0137 (5)	0.0148 (5)	0.0169 (5)	0.0016 (4)	0.0030 (4)	0.0016 (4)
C15	0.0138 (5)	0.0138 (5)	0.0183 (5)	0.0025 (4)	0.0027 (4)	0.0006 (4)
C16	0.0144 (5)	0.0129 (5)	0.0162 (5)	0.0023 (4)	0.0029 (4)	0.0011 (4)
C17	0.0138 (5)	0.0110 (4)	0.0194 (5)	0.0030 (4)	0.0023 (4)	0.0020 (4)
C18	0.0127 (4)	0.0108 (4)	0.0143 (5)	0.0006 (4)	0.0027 (3)	0.0010 (3)

Geometric parameters (Å, º)

O1—C18	1.2429 (13)	C6—H6A	0.9900
O2—C8	1.3710 (14)	C6—H6AB	0.9900
O2—C7	1.4400 (14)	C7—H00F	0.9900
O3—C9	1.3705 (14)	C7—H00G	0.9900
O3—C7	1.4372 (15)	C8—C13	1.3710 (15)
N1—C18	1.3440 (14)	C8—C9	1.3909 (15)
N1—C5	1.4614 (13)	C9—C10	1.3741 (16)
N1—H1	0.874 (16)	C10—C11	1.4028 (15)
C1—C2	1.5275 (16)	C10—H10	0.9500
C1—C6	1.5279 (16)	C11—C12	1.3991 (15)
C1—H1A	0.9900	C11—H11	0.9500
C1—H1AB	0.9900	C12—C13	1.4120 (15)
C2—C3	1.5246 (17)	C12—C14	1.4648 (15)
C2—H2A	0.9900	C13—H13	0.9500
C2—H2AB	0.9900	C14—C15	1.3468 (15)

C3—C4	1.5305 (16)	C14—H14	0.9500
C3—H3A	0.9900	C15—C16	1.4442 (15)
C3—H3AB	0.9900	C15—H15	0.9500
C4—C5	1.5284 (15)	C16—C17	1.3423 (15)
C4—H4A	0.9900	C16—H16	0.9500
C4—H4AB	0.9900	C17—C18	1.4793 (15)
C5—C6	1.5228 (15)	C17—H17	0.9500
C5—H5	1.0000		
C8—O2—C7	105.94 (9)	H6A—C6—H6AB	107.9
C9—O3—C7	106.11 (9)	O3—C7—O2	107.98 (9)
C18—N1—C5	123.36 (9)	O3—C7—H00F	110.1
C18—N1—H1	116.8 (10)	O2—C7—H00F	110.1
C5—N1—H1	119.9 (10)	O3—C7—H00G	110.1
C2—C1—C6	111.27 (9)	O2—C7—H00G	110.1
C2—C1—H1A	109.4	H00F—C7—H00G	108.4
C6—C1—H1A	109.4	C13—C8—O2	127.72 (10)
C2—C1—H1AB	109.4	C13—C8—C9	122.25 (10)
C6—C1—H1AB	109.4	O2—C8—C9	110.03 (10)
H1A—C1—H1AB	108.0	O3—C9—C10	128.10 (10)
C3—C2—C1	110.13 (9)	O3—C9—C8	109.91 (10)
C3—C2—H2A	109.6	C10—C9—C8	121.98 (10)
C1—C2—H2A	109.6	C9—C10—C11	116.43 (10)
C3—C2—H2AB	109.6	C9—C10—H10	121.8
C1—C2—H2AB	109.6	C11—C10—H10	121.8
H2A—C2—H2AB	108.1	C12—C11—C10	122.19 (11)
C2—C3—C4	111.23 (9)	C12—C11—H11	118.9
C2—C3—H3A	109.4	C10—C11—H11	118.9
C4—C3—H3A	109.4	C11—C12—C13	119.88 (10)
C2—C3—H3AB	109.4	C11—C12—C14	118.98 (10)
C4—C3—H3AB	109.4	C13—C12—C14	121.13 (10)
H3A—C3—H3AB	108.0	C8—C13—C12	117.22 (10)
C5—C4—C3	110.66 (9)	C8—C13—H13	121.4
C5—C4—H4A	109.5	C12—C13—H13	121.4
C3—C4—H4A	109.5	C15—C14—C12	125.40 (10)
C5—C4—H4AB	109.5	C15—C14—H14	117.3
C3—C4—H4AB	109.5	C12—C14—H14	117.3
H4A—C4—H4AB	108.1	C14—C15—C16	123.65 (11)
N1—C5—C6	108.34 (9)	C14—C15—H15	118.2
N1—C5—C4	111.98 (9)	C16—C15—H15	118.2
C6—C5—C4	111.37 (9)	C17—C16—C15	123.70 (10)
N1—C5—H5	108.3	C17—C16—H16	118.1
C6—C5—H5	108.3	C15—C16—H16	118.1
C4—C5—H5	108.3	C16—C17—C18	122.76 (10)
C5—C6—C1	111.66 (9)	C16—C17—H17	118.6
C5—C6—H6A	109.3	C18—C17—H17	118.6
C1—C6—H6A	109.3	O1—C18—N1	123.06 (10)
C5—C6—H6AB	109.3	O1—C18—C17	122.66 (10)

| C1—C6—H6AB | 109.3 | N1—C18—C17 | 114.26 (9) |

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1^i	0.874 (16)	2.086 (16)	2.9547 (12)	172.8 (14)

Symmetry code: (i) x, $y+1$, z.

5-(2H-1,3-Benzodioxol-5-yl)-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (II)

Crystal data

$C_{16}H_{17}NO_3$
$M_r = 271.30$
Orthorhombic, *Pbca*
$a = 11.8747$ (10) Å
$b = 7.2485$ (6) Å
$c = 30.392$ (2) Å
$V = 2616.0$ (4) Å^3
$Z = 8$
$F(000) = 1152$

$D_x = 1.378$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 3874 reflections
$\theta = 2.7$–25.8°
$\mu = 0.10$ mm^{-1}
$T = 90$ K
Needle, colorless
$0.28 \times 0.06 \times 0.06$ mm

Data collection

Bruker D8 goniometer
   diffractometer
Radiation source: microfocus X-ray tube
Multilayered conforacal mirror monochromator
Detector resolution: 7.391 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
   (SADABS; Bruker, 2018)
$T_{min} = 0.666$, $T_{max} = 0.746$

41504 measured reflections
3506 independent reflections
2193 reflections with $I > 2\sigma(I)$
$R_{int} = 0.128$
$\theta_{max} = 29.1°$, $\theta_{min} = 2.7°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -41 \rightarrow 41$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.143$
$S = 1.05$
3506 reflections
182 parameters
0 restraints
Hydrogen site location: inferred from
   neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 1.9223P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: SHELXL-2018/3
   (Sheldrick 2015b),
   $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0038 (6)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.90586 (12)	0.3421 (2)	0.67241 (5)	0.0219 (3)
O2	0.77314 (12)	0.9757 (2)	0.35830 (4)	0.0239 (4)
O3	0.62806 (12)	0.8589 (2)	0.40118 (5)	0.0238 (3)
N1	0.72232 (13)	0.3304 (2)	0.69173 (5)	0.0178 (4)
C1	0.80525 (16)	0.3650 (3)	0.66249 (6)	0.0179 (4)
C2	0.77084 (17)	0.4355 (3)	0.61881 (6)	0.0200 (4)
H2	0.693195	0.435608	0.611273	0.024*
C3	0.84580 (17)	0.4994 (3)	0.58954 (6)	0.0195 (4)
H3	0.923497	0.493700	0.596862	0.023*
C4	0.81458 (18)	0.5762 (3)	0.54755 (6)	0.0202 (4)
H4	0.737486	0.571321	0.539278	0.024*
C5	0.88758 (17)	0.6543 (3)	0.51932 (6)	0.0204 (4)
H5	0.964674	0.654787	0.527665	0.024*
C6	0.85964 (17)	0.7386 (3)	0.47701 (6)	0.0189 (4)
C7	0.94619 (18)	0.8085 (3)	0.45072 (7)	0.0233 (5)
H7	1.021461	0.801352	0.461170	0.028*
C8	0.92613 (18)	0.8889 (3)	0.40946 (7)	0.0238 (5)
H8	0.985763	0.934891	0.391755	0.029*
C9	0.81622 (17)	0.8975 (3)	0.39603 (6)	0.0197 (4)
C10	0.65583 (18)	0.9250 (3)	0.35806 (7)	0.0243 (5)
H10A	0.608744	1.033210	0.350559	0.029*
H10B	0.642106	0.827357	0.335911	0.029*
C11	0.72958 (17)	0.8288 (3)	0.42176 (6)	0.0192 (4)
C12	0.74749 (17)	0.7485 (3)	0.46174 (6)	0.0194 (4)
H12	0.686800	0.701056	0.478668	0.023*
C13	0.74989 (17)	0.2759 (3)	0.73696 (6)	0.0191 (4)
H13A	0.803365	0.364049	0.750477	0.023*
H13B	0.783182	0.150743	0.737737	0.023*
C14	0.63666 (17)	0.2799 (3)	0.76059 (7)	0.0214 (4)
H14A	0.633146	0.183869	0.783722	0.026*
H14B	0.622901	0.401963	0.774158	0.026*
C15	0.55179 (17)	0.2411 (3)	0.72417 (7)	0.0229 (5)
H15A	0.476464	0.289608	0.731974	0.028*
H15B	0.545712	0.107030	0.718398	0.028*
C16	0.59994 (16)	0.3421 (3)	0.68437 (7)	0.0202 (4)
H16A	0.578131	0.280454	0.656583	0.024*
H16B	0.574336	0.472052	0.683550	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0160 (7)	0.0250 (8)	0.0247 (7)	0.0012 (6)	−0.0006 (6)	0.0005 (6)
O2	0.0236 (8)	0.0286 (8)	0.0195 (7)	−0.0012 (6)	−0.0007 (6)	0.0050 (6)
O3	0.0196 (8)	0.0307 (8)	0.0209 (7)	0.0019 (6)	−0.0009 (6)	0.0048 (6)
N1	0.0134 (8)	0.0218 (9)	0.0181 (8)	−0.0001 (7)	−0.0008 (6)	0.0024 (7)

C1	0.0177 (10)	0.0158 (9)	0.0204 (10)	−0.0005 (8)	−0.0011 (8)	−0.0021 (8)
C2	0.0186 (10)	0.0206 (10)	0.0208 (10)	0.0005 (8)	−0.0025 (8)	−0.0014 (8)
C3	0.0199 (10)	0.0194 (10)	0.0191 (10)	0.0002 (8)	−0.0009 (8)	−0.0017 (8)
C4	0.0201 (10)	0.0201 (10)	0.0203 (10)	0.0012 (8)	−0.0022 (8)	−0.0017 (8)
C5	0.0181 (10)	0.0214 (10)	0.0216 (10)	0.0014 (8)	−0.0003 (8)	−0.0002 (8)
C6	0.0187 (10)	0.0197 (10)	0.0184 (10)	0.0013 (8)	0.0002 (8)	−0.0022 (8)
C7	0.0185 (10)	0.0283 (11)	0.0230 (10)	−0.0001 (9)	0.0006 (8)	0.0003 (9)
C8	0.0214 (11)	0.0265 (11)	0.0236 (10)	−0.0015 (9)	0.0048 (8)	0.0028 (9)
C9	0.0232 (11)	0.0204 (10)	0.0156 (9)	−0.0011 (8)	0.0008 (8)	0.0006 (8)
C10	0.0218 (11)	0.0308 (12)	0.0204 (10)	0.0001 (9)	−0.0006 (8)	0.0026 (9)
C11	0.0180 (10)	0.0197 (10)	0.0200 (10)	0.0009 (8)	−0.0011 (8)	−0.0004 (8)
C12	0.0182 (10)	0.0202 (10)	0.0197 (9)	−0.0001 (8)	0.0025 (8)	−0.0001 (8)
C13	0.0198 (10)	0.0196 (10)	0.0180 (9)	0.0017 (8)	−0.0007 (8)	0.0008 (8)
C14	0.0206 (10)	0.0218 (10)	0.0218 (10)	0.0007 (9)	0.0021 (8)	0.0008 (8)
C15	0.0171 (10)	0.0266 (11)	0.0251 (10)	−0.0011 (9)	0.0018 (8)	−0.0016 (9)
C16	0.0144 (9)	0.0241 (11)	0.0221 (10)	0.0011 (8)	−0.0007 (8)	0.0000 (8)

Geometric parameters (Å, º)

O1—C1	1.243 (2)	C7—H7	0.9500
O2—C9	1.377 (2)	C8—C9	1.369 (3)
O2—C10	1.441 (2)	C8—H8	0.9500
O3—C11	1.376 (2)	C9—C11	1.385 (3)
O3—C10	1.434 (2)	C10—H10A	0.9900
N1—C1	1.350 (2)	C10—H10B	0.9900
N1—C13	1.467 (2)	C11—C12	1.364 (3)
N1—C16	1.473 (2)	C12—H12	0.9500
C1—C2	1.480 (3)	C13—C14	1.525 (3)
C2—C3	1.341 (3)	C13—H13A	0.9900
C2—H2	0.9500	C13—H13B	0.9900
C3—C4	1.441 (3)	C14—C15	1.523 (3)
C3—H3	0.9500	C14—H14A	0.9900
C4—C5	1.345 (3)	C14—H14B	0.9900
C4—H4	0.9500	C15—C16	1.525 (3)
C5—C6	1.462 (3)	C15—H15A	0.9900
C5—H5	0.9500	C15—H15B	0.9900
C6—C7	1.397 (3)	C16—H16A	0.9900
C6—C12	1.412 (3)	C16—H16B	0.9900
C7—C8	1.403 (3)		

C9—O2—C10	104.98 (15)	O2—C10—H10A	110.2
C11—O3—C10	105.50 (15)	O3—C10—H10B	110.2
C1—N1—C13	120.26 (16)	O2—C10—H10B	110.2
C1—N1—C16	127.52 (16)	H10A—C10—H10B	108.5
C13—N1—C16	112.21 (15)	C12—C11—O3	127.55 (19)
O1—C1—N1	121.10 (18)	C12—C11—C9	122.74 (19)
O1—C1—C2	121.93 (18)	O3—C11—C9	109.69 (17)
N1—C1—C2	116.95 (17)	C11—C12—C6	117.50 (19)

C3—C2—C1	122.08 (19)	C11—C12—H12	121.3
C3—C2—H2	119.0	C6—C12—H12	121.3
C1—C2—H2	119.0	N1—C13—C14	103.86 (16)
C2—C3—C4	123.4 (2)	N1—C13—H13A	111.0
C2—C3—H3	118.3	C14—C13—H13A	111.0
C4—C3—H3	118.3	N1—C13—H13B	111.0
C5—C4—C3	124.2 (2)	C14—C13—H13B	111.0
C5—C4—H4	117.9	H13A—C13—H13B	109.0
C3—C4—H4	117.9	C15—C14—C13	103.75 (16)
C4—C5—C6	126.23 (19)	C15—C14—H14A	111.0
C4—C5—H5	116.9	C13—C14—H14A	111.0
C6—C5—H5	116.9	C15—C14—H14B	111.0
C7—C6—C12	119.16 (18)	C13—C14—H14B	111.0
C7—C6—C5	119.19 (18)	H14A—C14—H14B	109.0
C12—C6—C5	121.64 (18)	C14—C15—C16	103.87 (16)
C6—C7—C8	122.5 (2)	C14—C15—H15A	111.0
C6—C7—H7	118.8	C16—C15—H15A	111.0
C8—C7—H7	118.8	C14—C15—H15B	111.0
C9—C8—C7	116.59 (19)	C16—C15—H15B	111.0
C9—C8—H8	121.7	H15A—C15—H15B	109.0
C7—C8—H8	121.7	N1—C16—C15	102.81 (16)
C8—C9—O2	128.41 (18)	N1—C16—H16A	111.2
C8—C9—C11	121.54 (19)	C15—C16—H16A	111.2
O2—C9—C11	110.01 (18)	N1—C16—H16B	111.2
O3—C10—O2	107.62 (16)	C15—C16—H16B	111.2
O3—C10—H10A	110.2	H16A—C16—H16B	109.1