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2-(4-methoxyphenyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate:
crystal structure and Hirshfeld analysis**

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(1*R*,2*S*,5*R*)-5-Methyl-2-[2-(4-nitrophenyl)propan-2-yl]cyclohexyl 2-(4-methoxyphenyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate: crystal structure and Hirshfeld analysis

Julio Zukerman-Schpector,^{a*} Monica Soto-Monsalve,^b Regina H. De Almeida Santos,^b Angelo H. L. Machado,^{c‡} Carlos Roque D. Correia,^c Mukesh M. Jotani^d and Edward R. T. Tiekink^{e§}

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In the title compound, C₂₈H₃₄N₂O₅, the adjacent ester and nitrobenzene substituents are connected *via* an intramolecular methylene-C—H···π(nitrobenzene) interaction and the molecule approximates to a U-shape. The dihydropyrrole ring (r.m.s. deviation = 0.003 Å) is almost co-planar with the carboxylate residue [C_m—N—C1—O_c (m = methine, c = carboxyl) torsion angle = 1.8 (4)°] but is orthogonal to the 4-methoxybenzene ring [dihedral angle = 84.34 (17)°]. In the crystal, methylene-C—H···O(carbonyl) interactions lead to linear supramolecular chains along the *b*-axis direction, which pack without directional interactions between them. The analysis of the calculated Hirshfeld surface points to the importance of weak interatomic H···H, O···H/H···O and C···H/H···C contacts in the crystal.

1. Chemical context

The reaction of an unsaturated halide species with an alkene, in the presence of both a base and a organopalladium catalyst, to form a substituted alkene, is termed the Heck reaction (Heck, 1982; Crisp, 1998). As part of our investigations into the scope of the Heck reaction in the total, enantioselective and efficient synthesis of pyrrolidine alkaloids, such as the natural product (–)-codonopsinine (Severino & Correia, 2001), an enecarbamate containing the chiral auxiliary residue, 8-(4-nitrophenyl)menthol, was submitted to a Heck arylation reaction with 4-methoxyphenyldiazonium tetrafluoroborate. The reaction yielded the title compound, 8-(4-nitrophenyl)-menthyl 2-(4-methoxyphenyl)pyrroline-3-carboxylate, (I), as the sole crystalline material (Machado, 2001). Herein, the crystal and molecular structures of (I) are described along with an analysis of the calculated Hirshfeld surfaces.

2. Structural commentary

The molecular structure of (I), Fig. 1, comprises a 1-, 2- and 5-substituted cyclohexyl ring (chair conformation) with the chirality at these equatorially substituted centres, *i.e.* C14, C15 and C18, established from the synthesis, being *R*, *S* and *R*, respectively. The dihydropyrrole ring is essentially planar, with an r.m.s. deviation of 0.003 Å for the five constituent

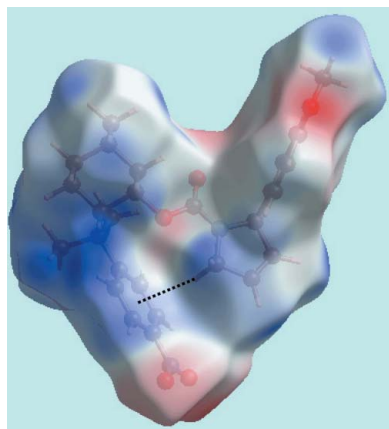


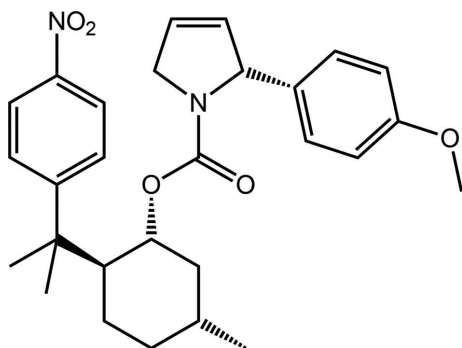
Table 1
Hydrogen-bond geometry (Å, °).

Cg1 is the ring centroid of the C24–C29 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>
C5–H5A...Cg1	0.97	2.67	3.612 (3)	163
C19–H19B...O2 ⁱ	0.97	2.60	3.472 (4)	150

Symmetry code: (i) *x*, *y* – 1, *z*.

atoms; the N1 and C5 atoms lie 0.037 (2) and 0.030 (3) Å to opposite sides of the plane. The chirality of the C2 centre is *R*. The carboxylate residue is almost co-planar with the five-membered pyrrole ring as seen in the value of the C2–N1–C13–O2 torsion angle of 1.8 (4)°. However, the appended 4-methoxybenzene ring is almost orthogonal to the pyrrole ring, forming a dihedral angle of 84.34 (17)°; the methoxy group is co-planar with the benzene ring with the C12–O3–C9–C10 torsion angle being 178.0 (4)°. In the same way, the nitro group is co-planar with the benzene ring to which it is connected with the O5–N2–C27–C28 torsion angle being 1.2 (5)°. In the molecule, there is a close pyrrole-methylene-C5–H... π (C24–C29) interaction, Table 1, which connects the substituents at the cyclohexyl-C14 and C15 atoms which lie to the same side of the molecule and which define a shape corresponding to the letter U.



3. Supramolecular features

The molecular packing of (I) features a number of weak non-covalent contacts as discussed below in the *Hirshfeld surface analysis* (§4). In accord with the distance criteria assumed in *PLATON* (Spek, 2009), there is only one directional interaction of note, Table 1. Thus, methylene-C19–H...O2(carbonyl) interactions connect molecules into a linear supramolecular chain along the *b*-axis direction, Fig. 2*a*. These assemble in the crystal with no directional interactions between them, Fig. 2*b*.

4. Hirshfeld surface analysis

The Hirshfeld surfaces calculated for (I) were conducted as reported recently for a related organic molecule (Zukerman-Schpector *et al.*, 2017) and provide information on the influence of short interatomic non-bonded contacts upon the molecular packing.

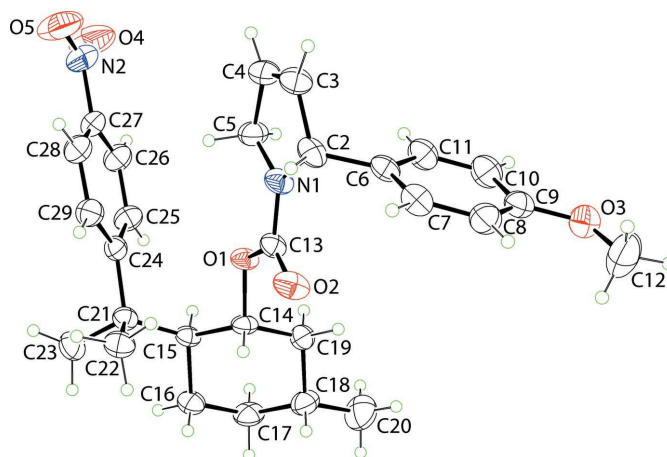


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

With reference to Fig. 3, in addition to the bright-red spots near the methylene-H19B and carbonyl-O2 atoms, representing the C–H...O interaction listed in Table 1, the diminutive-red spots near the O3, C9 and H17B atoms, corresponding to short interatomic O3...H17B and C9...H17B contacts (Table 2), on the Hirshfeld surface mapped over d_{norm} suggest they also have some influence on the molecular packing in the crystal. The effect of other short interatomic O...H/H...O and C...H/H...C contacts listed in

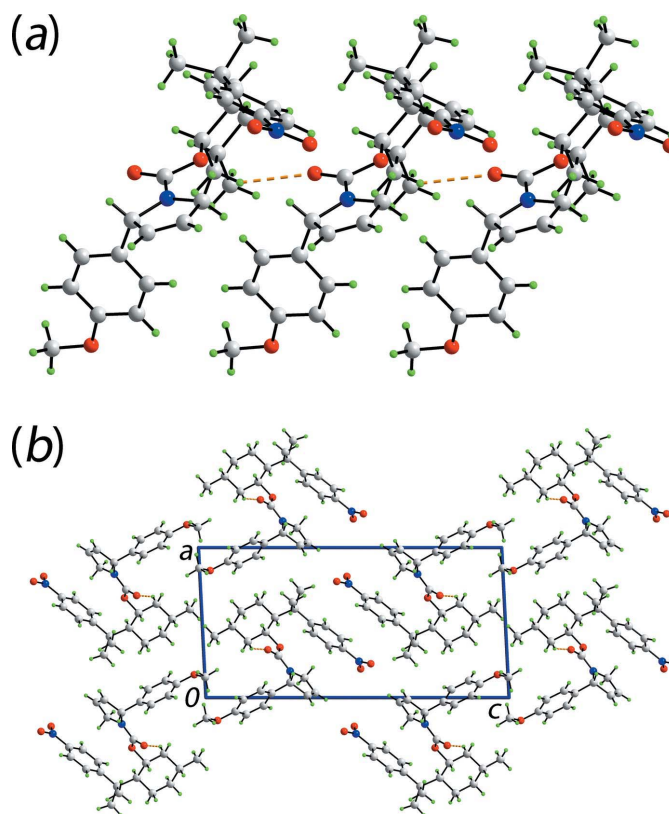


Figure 2
Molecular packing in (I): (a) view of the supramolecular chain along the *b* axis and (b) a view of the unit-cell contents shown in projection down the *b* axis. The C–H...O contacts are shown as orange dashed lines.

Table 2
 Summary of short interatomic contacts (Å) in (I).

Contact	Distance	Symmetry operation
H2...H5B	2.31	$x, 1 + y, z$
H7...H5B	2.28	$x, 1 + y, z$
H22A...H25	2.31	$x, 1 + y, z$
O3...H17B	2.52	$1 + x, 1 + y, z$
O3...H20B	2.56	$2 - x, -\frac{1}{2} + y, 2 - z$
O4...H4	2.56	$2 - x, -\frac{1}{2} + y, 1 - z$
O5...H22C	2.60	$1 - x, -\frac{1}{2} + y, 1 - z$
C9...H17B	2.72	$1 + x, 1 + y, z$
C9...H12C	2.80	$2 - x, -\frac{1}{2} + y, 2 - z$
C23...H3	2.84	$-1 + x, -1 + y, z$

Table 2 are also viewed as faint-red spots near the O3, H4, O5 and H20B atoms in Fig. 3. The influence of the short interatomic O...H, C...H and H...H contacts in the molecular packing are also illustrated in Fig. 4a and b, which show the Hirshfeld surface mapped over the shape-index property and d_{norm} , respectively. The intramolecular C—H... π contact between the pyrrole-H5A atom and the nitrobenzene ring [H5A...Cg(C24–C29) = 2.67 Å, C5...Cg(C24–C29) = 3.612 (3) Å and C—H5A...Cg(C24–C29) angle = 163°] is shown as a black-dotted line within the Hirshfeld surfaces mapped over the electrostatic potential in Fig. 5.

The overall two-dimensional fingerprint plot for (I), Fig. 6a, and those delineated into H...H, O...H/H...O and C...H/H...C contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 6b–d, respectively. The fingerprint plots also reflect the presence of the short interatomic contacts on the packing, Table 2. This is also evident from the percentage contribution from different interatomic contacts to the Hirshfeld surface summarized in Table 3: the H...H, O...H/H...O and C...H/H...C interatomic contacts make the greatest contribution to the Hirshfeld surface and account for 97.9% of the overall surface. The broad feather-like distribution of points with a peak at $d_e + d_i \sim 2.3$ Å in the fingerprint plot delineated into H...H contacts in Fig. 5b represent H...H contacts in the structure and make the greatest, *i.e.* 61.7%, contribution to the surface. The interatomic O...H/H...O contacts having a 23.9% contribution to the Hirshfeld surface arise from the C—H...O contact (Table 1) and short interatomic O...H/H...O

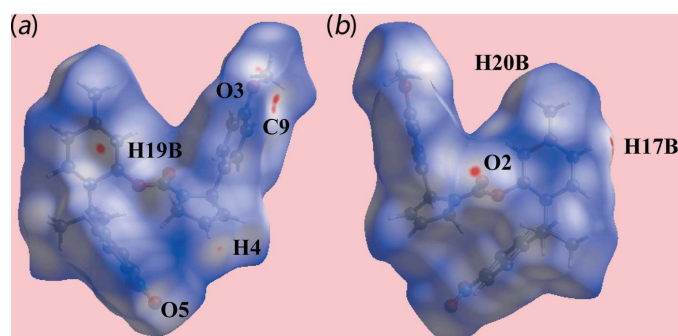
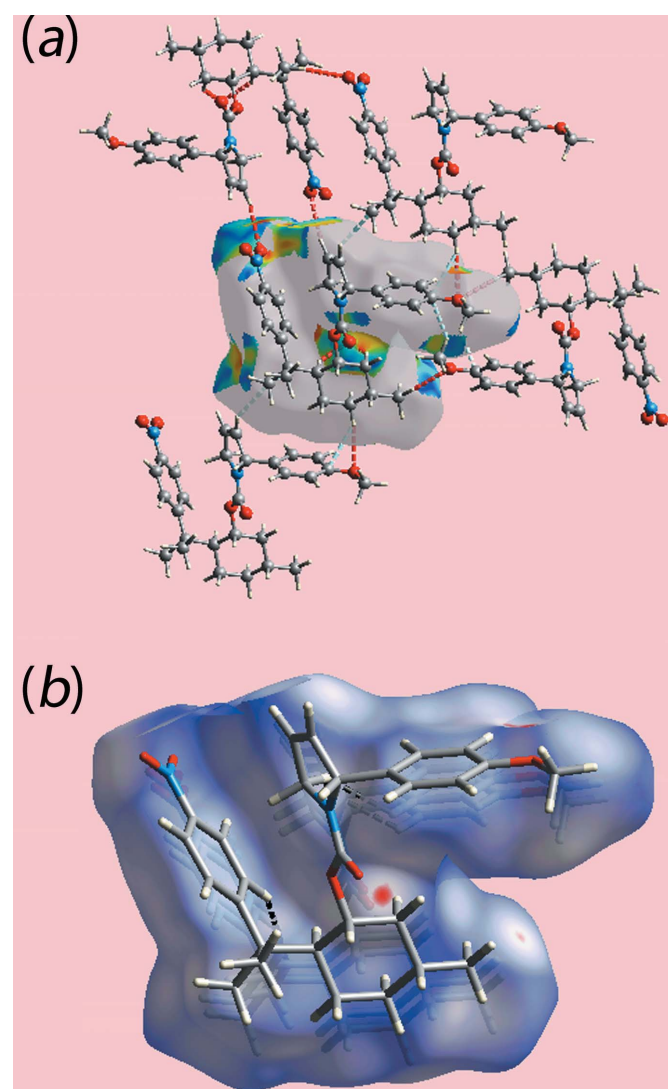
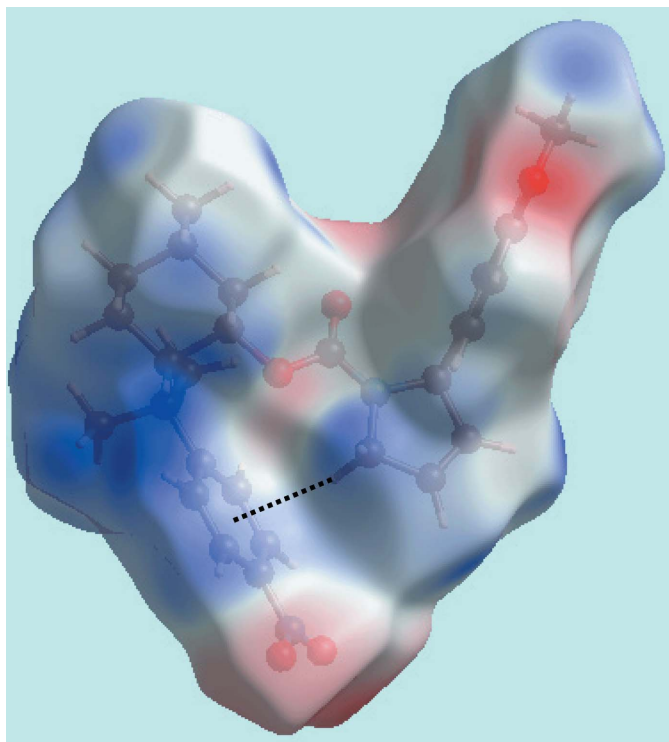

Figure 3
 Two views of the Hirshfeld surface for (I) mapped over d_{norm} in the range -0.071 to $+1.718$ au.

Table 3
 Percentage contributions of interatomic contacts to the Hirshfeld surface for (I).

Contact	Percentage contribution
H...H	61.7
O...H/H...O	23.9
C...H/H...C	12.3
N...H/H...N	1.1
O...O	0.7
C...O/O...C	0.2
C...C	0.1

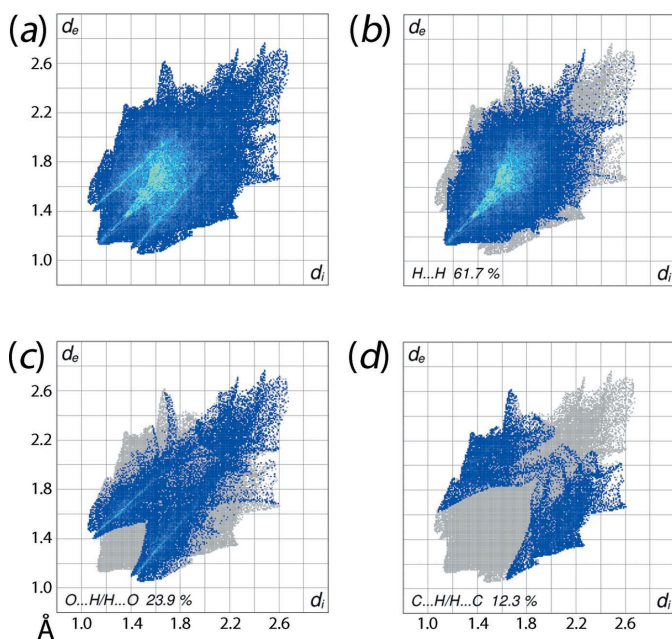
contacts (Table 2), and are viewed as the pair of green aligned points beginning at $d_e + d_i \sim 2.6$ Å and a pair of jaw-shaped distribution of points in the range $d_e + d_i \sim 2.5$ – 2.6 Å in Fig. 6c. The points distributed around the pair of forceps-like peaks at $d_e + d_i \sim 2.8$ Å in the fingerprint plot delineated into C...H/H...C contacts (Fig. 6d) represent the formation of such intra-


Figure 4
 Views of Hirshfeld surfaces mapped (a) with shape-index property highlighting short interatomic O...H/H...O and C...H/H...C contacts by red and sky-blue dashed lines, respectively, and (b) over d_{norm} showing intra-layer interatomic H...H contacts by black dashed lines.


Figure 5

A view of the Hirshfeld surface mapped over the electrostatic potential for (I) in the range -0.079 to $+0.038$ au, highlighting the intramolecular C–H $\cdots\pi$ contact by a black dotted line. The red and blue regions represent negative and positive electrostatic potentials, respectively.

and inter-layer contacts in the crystal. The small contribution from other interatomic contacts summarized in Table 3 appear to have a negligible impact on the molecular packing.


Figure 6

(a) The full two-dimensional fingerprint plot for (I) and fingerprint plots delineated into (b) H \cdots H, (c) O \cdots H/H \cdots O and (d) C \cdots H/H \cdots C contacts.

Table 4

Experimental details.

Crystal data	
Chemical formula	C ₂₈ H ₃₄ N ₂ O ₅
M_r	478.57
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	293
a, b, c (Å)	10.3142 (10), 6.1114 (8), 20.844 (3)
β (°)	92.83 (1)
V (Å ³)	1312.3 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.08
Crystal size (mm)	0.40 × 0.25 × 0.20
Data collection	
Diffractometer	Enraf–Nonius TurboCAD4
Absorption correction	ψ scan (CAD-4 EXPRESS; Enraf–Nonius, 1989)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4246, 4145, 2310
R_{int}	0.054
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.144, 0.98
No. of reflections	4145
No. of parameters	320
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.27, -0.16
Absolute structure	No quotients, so Flack parameter determined by classical intensity fit
Absolute structure parameter	-1.1 (16)

Computer programs: CAD-4 EXPRESS (Enraf–Nonius, 1989), XCAD4 (Harms & Wocadlo, 1995), SIR2014 (Burla *et al.*, 2015), SHELXL2014 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006), MarvinSketch (ChemAxon, 2010) and publCIF (Westrip, 2010).

5. Database survey

The (1*R*,2*S*,5*R*)-menthyl substrate is important as a chiral source for the synthesis of natural products and, as such, has been found in a number of crystal structures related to (I). Owing to the dictates of the chirality at the C1 and C2 positions, a parallel alignment of the substituents at these positions usually result in U-shaped geometries (Aoyagi *et al.*, 1998; Singh *et al.*, 1990; Streith *et al.*, 1995), except in circumstances where steric hindrance precludes such an arrangement (Comins & Killpack, 1992).

6. Synthesis and crystallization

As detailed previously (Machado, 2001), for the Heck arylation of (1*R*,2*S*,5*R*)-5-methyl-2-[2-(4-nitrophenyl)propan-2-yl]cyclohexyl 2,3-dihydro-1*H*-pyrrole-1-carboxylate, a stoichiometric quantity of 4-methoxyphenyldiazonium tetrafluoroborate was used along with 1 mol equivalent of Pd⁰ and 400 mol equivalent of sodium acetate. The reaction was conducted in acetonitrile at room temperature for 15 min, yielding (1*R*,2*S*,5*R*)-5-methyl-2-[2-(4-nitrophenyl)propan-2-yl]cyclohexyl (2*S*)-2-(4-methoxyphenyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate and the title compound, (I), the latter being the only crystalline product, obtained as irregular

colourless chunks by slow evaporation of an *n*-hexane–ethyl acetate solution (8:2 *v/v*). M.p 378–380 K. ESI–MS (*m/z*) calculated for C₂₈H₃₄N₂O₅ [*M*]⁺ 478.24677, found 478.24676. [α]_D²⁰ = +85.6 9c = 0.7; ethylacetate). *R*_F = 0.40 (hexane–ethyl acetate, 8:2 *v/v*).

The reported ¹H and ¹³C NMR reflect the presence of two conformational rotamers in solution. ¹H NMR (500 MHz, CCl₄): δ [8.01 (*d*, *J* = 9 Hz) + 7.94 (*d*, *J* = 9 Hz) = 2H]; [7.43 (*d*, *J* = 9 Hz) + 7.16 (*d*, *J* = 9 Hz) = 2H]; [7.05 (*d*, *J* = 9 Hz) + 7.00 (*d*, *J* = 9 Hz) = 2H]; [6.77 (*d*, *J* = 9 Hz) + 6.70 (*d*, *J* = 9 Hz) = 2H]; 5.88 (*br d*, *J* = 6 Hz) + 5.67–5.59 (*m*) = 1H]; [5.67–5.59 (*m*) + 5.51 (*dd*, *J* = 7 Hz, 1 Hz) = 1H]; [5.27 (*br s*) + 5.19 (*br s*) = 1H]; 4.70 (*td*, *J* = 10 Hz and 5 Hz, 1H); [4.36 (*br d*, *J* = 15 Hz) + 4.21 (*m*) + 3.53 (*dd*, *J* = 15 and 5 Hz) + 2.59 (*dd*, *J* = 15 and 2 Hz) = 2H]; [3.77 (*s*) + 3.72 (*s*) = 3H]; 2.04–0.49 (*m*, 11H); [1.43 (*s*) + 1.25 (*s*) = 3H]; [1.21 (*s*) + 1.11 (*s*) = 3H]. ¹³C NMR (75.5 MHz, CCl₄): δ 159.1, 158.5, 151.6, 132.2, 130.9, 130.5, 128.0, 127.8, 125.9, 125.5, 123.9, 123.7, 122.3, 113.3, 113.1, 95.8, 73.5, 72.7, 67.3, 66.8, 54.6, 54.3, 51.7, 51.5, 42.4, 39.9, 34.3, 31.1, 30.2, 29.4, 26.0, 21.6, 21.5.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. The C-bound H atoms were placed in calculated positions (C–H = 0.93–0.98 Å) and were included in the refinement in the riding model approximation, with *U*_{iso}(H) set to 1.2–1.5*U*_{eq}(C).

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Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: MarvinSketch (ChemAxon, 2010) and *publCIF* (Westrip, 2010).

(1*R*,2*S*,5*R*)-5-Methyl-2-[2-(4-nitrophenyl)propan-2-yl]cyclohexyl 2-(4-methoxyphenyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate

Crystal data

C₂₈H₃₄N₂O₅

M_r = 478.57

Monoclinic, *P*2₁

a = 10.3142 (10) Å

b = 6.1114 (8) Å

c = 20.844 (3) Å

β = 92.83 (1)°

V = 1312.3 (3) Å³

Z = 2

F(000) = 512

D_x = 1.211 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 11.8–18.2°

μ = 0.08 mm⁻¹

T = 293 K

Irregular, colourless

0.40 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius TurboCAD4
diffractometer

Radiation source: Enraf–Nonius FR590
non-profiled $\omega/2\theta$ scans

Absorption correction: ψ scan
(CAD-4 EXPRESS; Enraf–Nonius, 1989)

4246 measured reflections

4145 independent reflections

2310 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.054

θ_{\max} = 30.0°, θ_{\min} = 2.3°

h = -14→14

k = 0→8

l = -29→0

3 standard reflections every 60 min

intensity decay: 1%

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.056$ $wR(F^2) = 0.144$ $S = 0.98$

4145 reflections

320 parameters

1 restraint

Primary atom site location: structure-invariant
direct methodsHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$ Absolute structure: No quotients, so Flack
parameter determined by classical intensity fitAbsolute structure parameter: -1.1 (16)*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.8239 (2)	0.1157 (4)	0.71804 (11)	0.0477 (6)
N2	0.7587 (3)	-0.3619 (8)	0.48894 (14)	0.0797 (11)
O1	0.66501 (17)	-0.1036 (3)	0.74757 (9)	0.0433 (5)
O2	0.6807 (2)	0.2399 (4)	0.78790 (11)	0.0609 (6)
O3	1.1526 (2)	0.4302 (5)	0.96516 (11)	0.0708 (7)
O4	0.8084 (4)	-0.5387 (8)	0.48479 (16)	0.1195 (13)
O5	0.7743 (3)	-0.2175 (7)	0.45058 (14)	0.1154 (13)
C2	0.9005 (3)	0.3194 (5)	0.71908 (15)	0.0505 (8)
H2	0.8431	0.4434	0.7086	0.061*
C3	0.9859 (3)	0.2781 (7)	0.66428 (16)	0.0667 (10)
H3	1.0448	0.3799	0.6498	0.080*
C4	0.9688 (3)	0.0841 (8)	0.63905 (16)	0.0678 (11)
H4	1.0140	0.0321	0.6047	0.081*
C5	0.8683 (3)	-0.0446 (6)	0.67187 (15)	0.0553 (8)
H5A	0.7983	-0.0899	0.6420	0.066*
H5B	0.9055	-0.1725	0.6933	0.066*
C6	0.9711 (3)	0.3593 (5)	0.78309 (15)	0.0475 (7)
C7	0.9543 (3)	0.5462 (6)	0.81758 (16)	0.0564 (8)
H7	0.9012	0.6560	0.7999	0.068*
C8	1.0136 (3)	0.5782 (6)	0.87811 (16)	0.0605 (9)
H8	1.0002	0.7076	0.9003	0.073*
C9	1.0914 (3)	0.4197 (6)	0.90480 (15)	0.0546 (8)
C10	1.1126 (3)	0.2279 (7)	0.87032 (17)	0.0638 (9)
H10	1.1667	0.1196	0.8880	0.077*
C11	1.0541 (3)	0.1994 (6)	0.81092 (16)	0.0574 (8)
H11	1.0693	0.0715	0.7883	0.069*
C12	1.1372 (5)	0.6248 (10)	1.0010 (2)	0.1029 (17)
H12A	1.1692	0.7469	0.9775	0.154*

H12B	1.1851	0.6128	1.0415	0.154*
H12C	1.0469	0.6465	1.0082	0.154*
C13	0.7197 (3)	0.0966 (5)	0.75437 (13)	0.0409 (6)
C14	0.5631 (2)	-0.1508 (5)	0.79199 (12)	0.0399 (6)
H14	0.5190	-0.0143	0.8024	0.048*
C15	0.4655 (2)	-0.3067 (5)	0.75898 (12)	0.0386 (6)
H15	0.5117	-0.4430	0.7505	0.046*
C16	0.3628 (3)	-0.3597 (7)	0.80803 (14)	0.0563 (8)
H16A	0.3163	-0.2271	0.8181	0.068*
H16B	0.3006	-0.4633	0.7892	0.068*
C17	0.4248 (3)	-0.4550 (6)	0.86912 (15)	0.0604 (9)
H17A	0.4659	-0.5927	0.8592	0.072*
H17B	0.3576	-0.4852	0.8989	0.072*
C18	0.5250 (3)	-0.3043 (6)	0.90138 (13)	0.0568 (8)
H18	0.4813	-0.1693	0.9135	0.068*
C19	0.6253 (3)	-0.2468 (6)	0.85248 (13)	0.0474 (7)
H19A	0.6868	-0.1424	0.8715	0.057*
H19B	0.6729	-0.3777	0.8418	0.057*
C20	0.5893 (4)	-0.4048 (9)	0.96163 (17)	0.0898 (14)
H20A	0.5242	-0.4410	0.9912	0.135*
H20B	0.6493	-0.3018	0.9813	0.135*
H20C	0.6351	-0.5350	0.9504	0.135*
C21	0.4069 (3)	-0.2208 (5)	0.69281 (13)	0.0416 (6)
C22	0.3634 (3)	0.0191 (5)	0.69810 (16)	0.0530 (8)
H22A	0.4380	0.1103	0.7068	0.079*
H22B	0.3051	0.0330	0.7323	0.079*
H22C	0.3201	0.0636	0.6584	0.079*
C23	0.2859 (3)	-0.3568 (6)	0.67073 (15)	0.0565 (8)
H23A	0.2172	-0.3298	0.6991	0.085*
H23B	0.3075	-0.5096	0.6716	0.085*
H23C	0.2582	-0.3151	0.6278	0.085*
C24	0.5042 (2)	-0.2514 (5)	0.63983 (12)	0.0415 (6)
C25	0.5699 (3)	-0.4489 (5)	0.63403 (14)	0.0511 (7)
H25	0.5574	-0.5593	0.6638	0.061*
C26	0.6534 (3)	-0.4855 (6)	0.58506 (14)	0.0573 (8)
H26	0.6975	-0.6177	0.5822	0.069*
C27	0.6697 (3)	-0.3229 (7)	0.54084 (13)	0.0557 (8)
C28	0.6056 (3)	-0.1281 (7)	0.54376 (14)	0.0608 (9)
H28	0.6167	-0.0207	0.5129	0.073*
C29	0.5237 (3)	-0.0928 (6)	0.59349 (14)	0.0530 (8)
H29	0.4806	0.0405	0.5959	0.064*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0418 (12)	0.0409 (14)	0.0610 (14)	-0.0140 (12)	0.0090 (11)	-0.0041 (13)
N2	0.078 (2)	0.115 (3)	0.0474 (16)	0.007 (2)	0.0169 (14)	-0.005 (2)
O1	0.0397 (10)	0.0395 (11)	0.0520 (10)	-0.0127 (9)	0.0150 (8)	-0.0037 (9)

O2	0.0527 (12)	0.0405 (12)	0.0911 (16)	-0.0101 (11)	0.0204 (11)	-0.0158 (13)
O3	0.0637 (13)	0.088 (2)	0.0603 (13)	-0.0025 (15)	-0.0009 (11)	0.0014 (14)
O4	0.141 (3)	0.129 (3)	0.094 (2)	0.037 (3)	0.059 (2)	-0.009 (2)
O5	0.131 (3)	0.142 (3)	0.0780 (19)	0.015 (3)	0.0538 (19)	0.027 (2)
C2	0.0430 (15)	0.0399 (17)	0.0684 (19)	-0.0163 (13)	-0.0002 (14)	0.0094 (14)
C3	0.0557 (19)	0.082 (3)	0.064 (2)	-0.034 (2)	0.0138 (16)	0.015 (2)
C4	0.0537 (18)	0.094 (3)	0.0569 (19)	-0.024 (2)	0.0169 (15)	0.004 (2)
C5	0.0540 (17)	0.060 (2)	0.0531 (16)	-0.0135 (17)	0.0160 (14)	-0.0087 (16)
C6	0.0368 (14)	0.0436 (17)	0.0625 (17)	-0.0125 (13)	0.0072 (12)	0.0034 (15)
C7	0.0477 (16)	0.051 (2)	0.070 (2)	-0.0005 (15)	0.0012 (15)	0.0039 (17)
C8	0.0575 (18)	0.059 (2)	0.0652 (19)	0.0002 (17)	0.0066 (15)	-0.0121 (18)
C9	0.0442 (15)	0.065 (2)	0.0552 (17)	-0.0055 (17)	0.0070 (13)	0.0046 (17)
C10	0.0536 (18)	0.060 (2)	0.077 (2)	0.0071 (18)	-0.0029 (17)	0.004 (2)
C11	0.0509 (16)	0.0486 (19)	0.072 (2)	-0.0037 (16)	0.0005 (15)	-0.0021 (17)
C12	0.127 (4)	0.110 (4)	0.070 (3)	0.007 (4)	-0.014 (3)	-0.028 (3)
C13	0.0362 (13)	0.0360 (15)	0.0506 (15)	-0.0067 (12)	0.0046 (11)	-0.0015 (13)
C14	0.0367 (13)	0.0397 (15)	0.0445 (14)	-0.0087 (12)	0.0159 (11)	-0.0044 (13)
C15	0.0331 (12)	0.0370 (15)	0.0466 (14)	-0.0065 (11)	0.0099 (10)	-0.0013 (12)
C16	0.0427 (15)	0.070 (2)	0.0573 (17)	-0.0166 (16)	0.0125 (13)	-0.0001 (18)
C17	0.0599 (18)	0.066 (2)	0.0576 (18)	-0.0162 (18)	0.0227 (15)	0.0081 (17)
C18	0.0626 (18)	0.064 (2)	0.0447 (15)	-0.0054 (17)	0.0128 (13)	0.0004 (16)
C19	0.0435 (14)	0.0507 (18)	0.0480 (15)	-0.0111 (14)	0.0032 (12)	-0.0050 (15)
C20	0.101 (3)	0.106 (4)	0.062 (2)	-0.016 (3)	0.002 (2)	0.021 (3)
C21	0.0383 (13)	0.0396 (16)	0.0470 (15)	-0.0021 (12)	0.0050 (12)	-0.0028 (13)
C22	0.0511 (17)	0.0450 (18)	0.0636 (18)	0.0069 (14)	0.0104 (15)	0.0012 (16)
C23	0.0448 (15)	0.060 (2)	0.0637 (18)	-0.0143 (15)	-0.0027 (13)	0.0000 (17)
C24	0.0393 (14)	0.0444 (16)	0.0406 (14)	-0.0068 (13)	-0.0005 (11)	-0.0010 (13)
C25	0.0631 (18)	0.0438 (17)	0.0472 (15)	-0.0021 (15)	0.0103 (14)	0.0015 (14)
C26	0.0671 (19)	0.0546 (19)	0.0504 (16)	0.0024 (17)	0.0063 (15)	-0.0097 (16)
C27	0.0545 (16)	0.078 (2)	0.0349 (14)	-0.0034 (18)	0.0029 (12)	-0.0059 (16)
C28	0.0618 (19)	0.075 (3)	0.0455 (16)	-0.0021 (19)	0.0035 (15)	0.0150 (18)
C29	0.0536 (16)	0.054 (2)	0.0516 (16)	0.0037 (16)	0.0034 (13)	0.0093 (16)

Geometric parameters (Å, °)

N1—C13	1.350 (3)	C15—C16	1.543 (4)
N1—C5	1.463 (4)	C15—C21	1.569 (4)
N1—C2	1.474 (4)	C15—H15	0.9800
N2—O4	1.201 (5)	C16—C17	1.513 (4)
N2—O5	1.207 (5)	C16—H16A	0.9700
N2—C27	1.473 (4)	C16—H16B	0.9700
O1—C13	1.352 (3)	C17—C18	1.517 (5)
O1—C14	1.463 (3)	C17—H17A	0.9700
O2—C13	1.202 (3)	C17—H17B	0.9700
O3—C9	1.381 (4)	C18—C20	1.520 (5)
O3—C12	1.417 (6)	C18—C19	1.529 (4)
C2—C3	1.498 (5)	C18—H18	0.9800
C2—C6	1.508 (4)	C19—H19A	0.9700

C2—H2	0.9800	C19—H19B	0.9700
C3—C4	1.306 (6)	C20—H20A	0.9600
C3—H3	0.9300	C20—H20B	0.9600
C4—C5	1.494 (4)	C20—H20C	0.9600
C4—H4	0.9300	C21—C22	1.539 (4)
C5—H5A	0.9700	C21—C24	1.540 (4)
C5—H5B	0.9700	C21—C23	1.550 (4)
C6—C7	1.365 (5)	C22—H22A	0.9600
C6—C11	1.405 (4)	C22—H22B	0.9600
C7—C8	1.389 (4)	C22—H22C	0.9600
C7—H7	0.9300	C23—H23A	0.9600
C8—C9	1.359 (5)	C23—H23B	0.9600
C8—H8	0.9300	C23—H23C	0.9600
C9—C10	1.398 (5)	C24—C29	1.390 (4)
C10—C11	1.361 (5)	C24—C25	1.393 (4)
C10—H10	0.9300	C25—C26	1.386 (4)
C11—H11	0.9300	C25—H25	0.9300
C12—H12A	0.9600	C26—C27	1.371 (5)
C12—H12B	0.9600	C26—H26	0.9300
C12—H12C	0.9600	C27—C28	1.365 (6)
C14—C19	1.505 (4)	C28—C29	1.386 (4)
C14—C15	1.525 (4)	C28—H28	0.9300
C14—H14	0.9800	C29—H29	0.9300
C13—N1—C5	126.5 (2)	C17—C16—H16A	109.4
C13—N1—C2	120.4 (2)	C15—C16—H16A	109.4
C5—N1—C2	113.0 (2)	C17—C16—H16B	109.4
O4—N2—O5	122.6 (4)	C15—C16—H16B	109.4
O4—N2—C27	118.8 (4)	H16A—C16—H16B	108.0
O5—N2—C27	118.5 (4)	C16—C17—C18	113.0 (3)
C13—O1—C14	114.9 (2)	C16—C17—H17A	109.0
C9—O3—C12	117.4 (3)	C18—C17—H17A	109.0
N1—C2—C3	100.5 (3)	C16—C17—H17B	109.0
N1—C2—C6	112.6 (2)	C18—C17—H17B	109.0
C3—C2—C6	115.2 (2)	H17A—C17—H17B	107.8
N1—C2—H2	109.4	C17—C18—C20	112.4 (3)
C3—C2—H2	109.4	C17—C18—C19	108.2 (2)
C6—C2—H2	109.4	C20—C18—C19	111.2 (3)
C4—C3—C2	112.8 (3)	C17—C18—H18	108.3
C4—C3—H3	123.6	C20—C18—H18	108.3
C2—C3—H3	123.6	C19—C18—H18	108.3
C3—C4—C5	112.1 (3)	C14—C19—C18	111.9 (2)
C3—C4—H4	123.9	C14—C19—H19A	109.2
C5—C4—H4	123.9	C18—C19—H19A	109.2
N1—C5—C4	101.3 (3)	C14—C19—H19B	109.2
N1—C5—H5A	111.5	C18—C19—H19B	109.2
C4—C5—H5A	111.5	H19A—C19—H19B	107.9
N1—C5—H5B	111.5	C18—C20—H20A	109.5

C4—C5—H5B	111.5	C18—C20—H20B	109.5
H5A—C5—H5B	109.3	H20A—C20—H20B	109.5
C7—C6—C11	117.1 (3)	C18—C20—H20C	109.5
C7—C6—C2	122.2 (3)	H20A—C20—H20C	109.5
C11—C6—C2	120.7 (3)	H20B—C20—H20C	109.5
C6—C7—C8	122.3 (3)	C22—C21—C24	111.7 (2)
C6—C7—H7	118.8	C22—C21—C23	107.4 (3)
C8—C7—H7	118.8	C24—C21—C23	105.4 (2)
C9—C8—C7	119.8 (3)	C22—C21—C15	110.9 (3)
C9—C8—H8	120.1	C24—C21—C15	110.7 (2)
C7—C8—H8	120.1	C23—C21—C15	110.6 (2)
C8—C9—O3	125.0 (3)	C21—C22—H22A	109.5
C8—C9—C10	119.4 (3)	C21—C22—H22B	109.5
O3—C9—C10	115.6 (3)	H22A—C22—H22B	109.5
C11—C10—C9	120.1 (3)	C21—C22—H22C	109.5
C11—C10—H10	119.9	H22A—C22—H22C	109.5
C9—C10—H10	119.9	H22B—C22—H22C	109.5
C10—C11—C6	121.3 (3)	C21—C23—H23A	109.5
C10—C11—H11	119.3	C21—C23—H23B	109.5
C6—C11—H11	119.3	H23A—C23—H23B	109.5
O3—C12—H12A	109.5	C21—C23—H23C	109.5
O3—C12—H12B	109.5	H23A—C23—H23C	109.5
H12A—C12—H12B	109.5	H23B—C23—H23C	109.5
O3—C12—H12C	109.5	C29—C24—C25	117.2 (2)
H12A—C12—H12C	109.5	C29—C24—C21	122.4 (3)
H12B—C12—H12C	109.5	C25—C24—C21	120.3 (3)
O2—C13—N1	124.1 (3)	C26—C25—C24	121.8 (3)
O2—C13—O1	124.8 (2)	C26—C25—H25	119.1
N1—C13—O1	111.1 (2)	C24—C25—H25	119.1
O1—C14—C19	108.5 (2)	C27—C26—C25	118.6 (3)
O1—C14—C15	108.43 (19)	C27—C26—H26	120.7
C19—C14—C15	112.3 (2)	C25—C26—H26	120.7
O1—C14—H14	109.2	C28—C27—C26	121.8 (3)
C19—C14—H14	109.2	C28—C27—N2	119.7 (3)
C15—C14—H14	109.2	C26—C27—N2	118.5 (4)
C14—C15—C16	107.0 (2)	C27—C28—C29	118.9 (3)
C14—C15—C21	113.9 (2)	C27—C28—H28	120.5
C16—C15—C21	113.9 (2)	C29—C28—H28	120.5
C14—C15—H15	107.2	C28—C29—C24	121.7 (3)
C16—C15—H15	107.2	C28—C29—H29	119.2
C21—C15—H15	107.2	C24—C29—H29	119.2
C17—C16—C15	111.3 (2)		
C13—N1—C2—C3	-170.1 (3)	C19—C14—C15—C21	-175.3 (2)
C5—N1—C2—C3	6.0 (3)	C14—C15—C16—C17	-56.9 (4)
C13—N1—C2—C6	66.8 (3)	C21—C15—C16—C17	176.4 (3)
C5—N1—C2—C6	-117.1 (3)	C15—C16—C17—C18	58.3 (4)
N1—C2—C3—C4	-3.6 (4)	C16—C17—C18—C20	-178.3 (3)

C6—C2—C3—C4	117.7 (4)	C16—C17—C18—C19	-55.1 (4)
C2—C3—C4—C5	0.0 (5)	O1—C14—C19—C18	-179.1 (2)
C13—N1—C5—C4	169.8 (3)	C15—C14—C19—C18	-59.3 (3)
C2—N1—C5—C4	-6.0 (3)	C17—C18—C19—C14	55.0 (4)
C3—C4—C5—N1	3.6 (4)	C20—C18—C19—C14	179.0 (3)
N1—C2—C6—C7	-123.2 (3)	C14—C15—C21—C22	-46.9 (3)
C3—C2—C6—C7	122.4 (3)	C16—C15—C21—C22	76.2 (3)
N1—C2—C6—C11	54.4 (4)	C14—C15—C21—C24	77.7 (3)
C3—C2—C6—C11	-60.1 (4)	C16—C15—C21—C24	-159.3 (3)
C11—C6—C7—C8	-1.3 (4)	C14—C15—C21—C23	-165.9 (2)
C2—C6—C7—C8	176.4 (3)	C16—C15—C21—C23	-42.8 (3)
C6—C7—C8—C9	-0.1 (5)	C22—C21—C24—C29	-14.5 (4)
C7—C8—C9—O3	-178.1 (3)	C23—C21—C24—C29	101.8 (3)
C7—C8—C9—C10	1.2 (5)	C15—C21—C24—C29	-138.6 (3)
C12—O3—C9—C8	-2.7 (5)	C22—C21—C24—C25	170.2 (3)
C12—O3—C9—C10	178.0 (4)	C23—C21—C24—C25	-73.5 (3)
C8—C9—C10—C11	-0.9 (5)	C15—C21—C24—C25	46.1 (3)
O3—C9—C10—C11	178.4 (3)	C29—C24—C25—C26	1.3 (4)
C9—C10—C11—C6	-0.4 (5)	C21—C24—C25—C26	176.9 (3)
C7—C6—C11—C10	1.5 (4)	C24—C25—C26—C27	-0.9 (5)
C2—C6—C11—C10	-176.2 (3)	C25—C26—C27—C28	-0.3 (5)
C5—N1—C13—O2	-173.7 (3)	C25—C26—C27—N2	179.8 (3)
C2—N1—C13—O2	1.8 (4)	O4—N2—C27—C28	-175.6 (4)
C5—N1—C13—O1	5.8 (4)	O5—N2—C27—C28	1.2 (5)
C2—N1—C13—O1	-178.7 (2)	O4—N2—C27—C26	4.2 (5)
C14—O1—C13—O2	-8.9 (4)	O5—N2—C27—C26	-179.0 (4)
C14—O1—C13—N1	171.6 (2)	C26—C27—C28—C29	1.1 (5)
C13—O1—C14—C19	-88.2 (3)	N2—C27—C28—C29	-179.0 (3)
C13—O1—C14—C15	149.6 (2)	C27—C28—C29—C24	-0.7 (5)
O1—C14—C15—C16	177.8 (2)	C25—C24—C29—C28	-0.5 (4)
C19—C14—C15—C16	58.0 (3)	C21—C24—C29—C28	-175.9 (3)
O1—C14—C15—C21	-55.4 (3)		

Hydrogen-bond geometry (Å, °)

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

Cg1 is the ring centroid of the C24–C29 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>
C5—H5 <i>A</i> ...Cg1	0.97	2.67	3.612 (3)	163
C19—H19 <i>B</i> ...O2 ⁱ	0.97	2.60	3.472 (4)	150

Symmetry code: (i) *x*, *y*-1, *z*.