

Crystal structure and Hirshfeld surface analysis of 5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide

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In the title compound, C₂₄H₃₁N₃O₂, the mean plane of the central pyrazole ring [r.m.s. deviation = 0.095 Å] makes dihedral angles of 11.93 (9) and 84.53 (8)°, respectively, with the phenyl and benzene rings. There is a short intramolecular N—H···N contact, which generates an *S*(5) ring motif. In the crystal, pairs of N—H···O hydrogen bonds link inversion-related molecules into dimers, generating an *R*₂²(8) ring motif. The Hirshfeld surface analysis indicates that the most significant contribution involves H···H contacts of 68.6%

1. Chemical context

Compounds containing the pyrazole ring system, considered to be a pharmacologically important active scaffold, possess diverse biological activities such as antimicrobial, anti-inflammatory, analgesic, anticonvulsant, anticancer, anthelmintic, antioxidant and herbicidal (Ansari *et al.*, 2017; Karrouchi *et al.*, 2018; Mamedov *et al.*, 2017). Such compounds have been the subject of NMR investigations of hydrogen bonding and keto–enol tautomerism in solution (Mamedov *et al.*, 2013, 2015). The structural properties of a series of compounds derived from 2,6-di-*tert*-butylphenol have been characterized in the solid state (Asgarova *et al.*, 2011*a,b*, 2019; Khalilov *et al.*, 2018*a,b*). Non-covalent bond donor/acceptor properties of pyrazoles or related N-compounds are crucial in the organization of supramolecular architectures in the solid state and hence their catalytic activity, solubility, *etc.* (Ma *et al.*, 2017; Maharramov *et al.*, 2010; Mahmoudi *et al.*, 2016, 2017*a,b*, 2018*a,b,c*; Mahmudov *et al.*, 2014, 2019; Shikhaliyev *et al.*, 2018). As part of a further study of this class of compounds, the crystal structure and Hirshfeld surface analysis of the title compound, 5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide, are reported on herein.

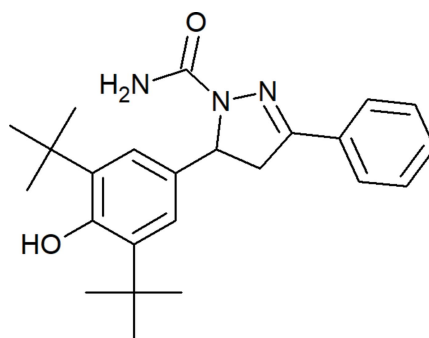
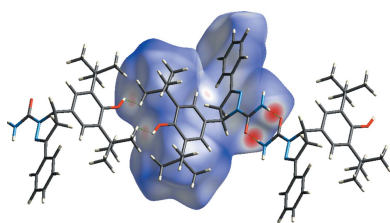


Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N28—H28B···N19	0.91 (2)	2.30 (2)	2.678 (3)	105 (2)
N28—H28A···O29 ⁱ	0.88 (2)	2.03 (2)	2.912 (3)	174 (2)

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

2. Structural commentary

As shown in Fig. 1, the title molecule contains three rings, pyrazole ring *A* (N19/N20/C16–C18; twisted conformation on bond C16–C17), phenyl ring *B* (C21–C26) and benzene ring *C* (C1–C6), with rings *B* and *C* being inclined to the mean plane of the central pyrazole ring *A* [r.m.s deviation = 0.095 Å] by 11.93 (9) and 84.53 (8)°, respectively. In the >NC(=O)NH₂ group, atoms N20, C27, O29 and N28 are coplanar, with N19–N20–C27–N28 and N19–N20–C27–O29 torsion angles of 4.0 (2) and –176.1 (1)°. All bond lengths and angles are comparable with those found for closely related structures, for example, methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Li *et al.*, 2014), 2,6-di-*tert*-butyl-4-methylphenol (Imura *et al.*, 1983), 2,6-di-*tert*-butyl-4-(3-chloro-2-hydroxypropyl)phenol (Asgarova *et al.*, 2011a) and 4-[3-(benzylamino)-2-hydroxypropyl]-2,6-di-*tert*-butylphenol (Asgarova *et al.*, 2011b). In the molecule, there is an N–H···N short contact, which generates an *S*(5) ring motif (Table 1).

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, pairs of N–H···O hydrogen bonds link inversion-related molecules into dimers, generating an *R*₂²(8) ring motif (Table 1; Fig. 2). No C–H···π or π–π interactions are present in the crystal structure (PLATON; Spek, 2009).

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was generated by *CrystalExplorer17* (Turner *et al.*, 2017) and comprises *d*_{norm} surface plots and two-dimensional

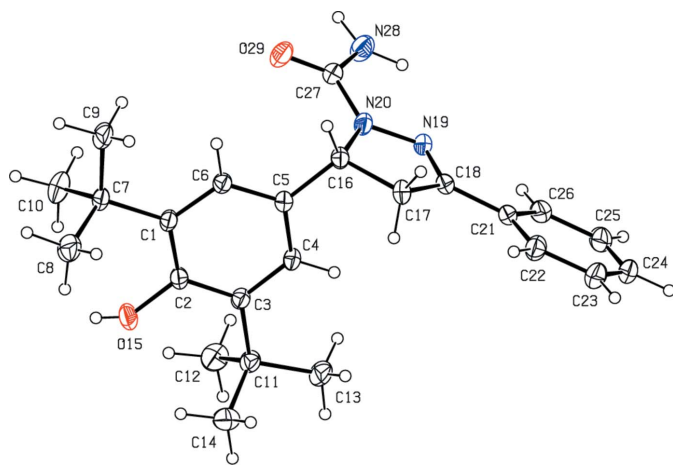


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

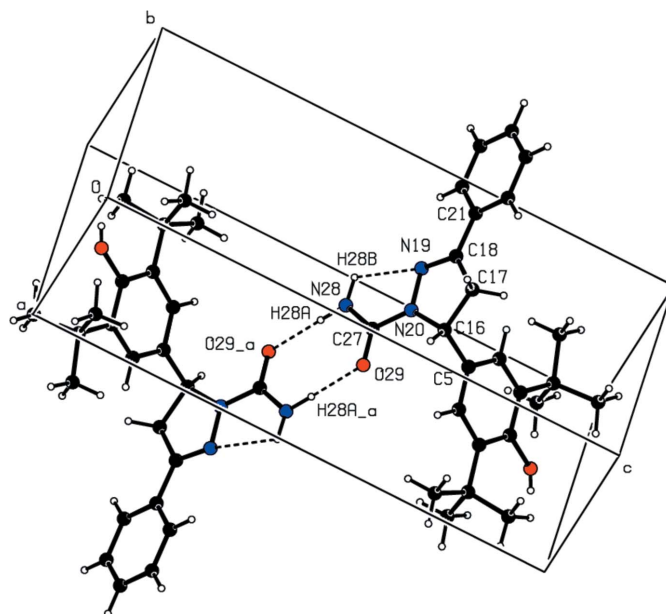


Figure 2
A view of the dimeric molecular bonding formed by N–H···O hydrogen bonds and N–H···N short contacts (dashed lines), with an *S*(5)*R*₂²(8)*S*(5) motif [symmetry code: (a) $-x + 2, -y + 1, -z + 1$].

fingerprint plots (Spackman & McKinnon, 2002). A *d*_{norm} surface plot of the title compound mapped using a standard surface resolution with a fixed colour scale of –0.5426 (red) to 1.7721 a.u. (blue) is shown in Fig. 3. The dark-red spots on the *d*_{norm} surface arise as a result of the N–H···O hydrogen bonds (Table 1), while the other weaker intermolecular interactions appear as light-red spots. The bright-red spots indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the Hirshfeld surfaces mapped over electrostatic potential (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005), as shown in Fig. 4.

The shape-index of the Hirshfeld surface is a tool to visualize π–π stacking interactions by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue

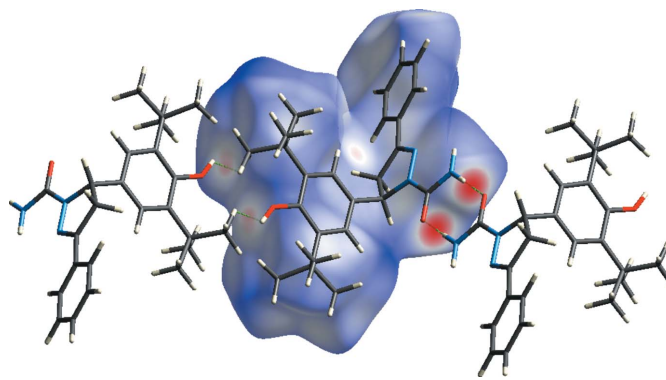
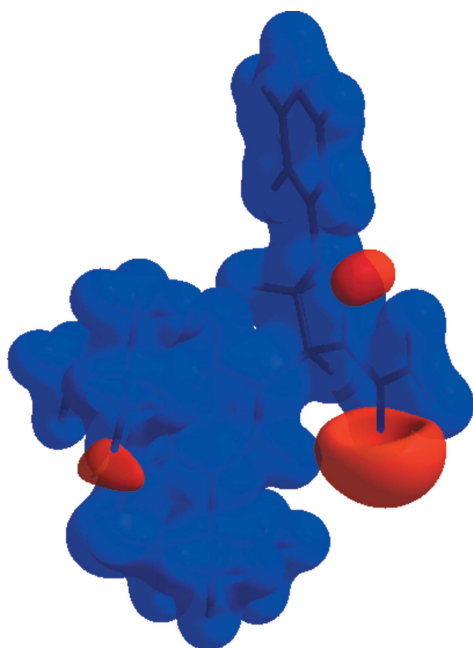
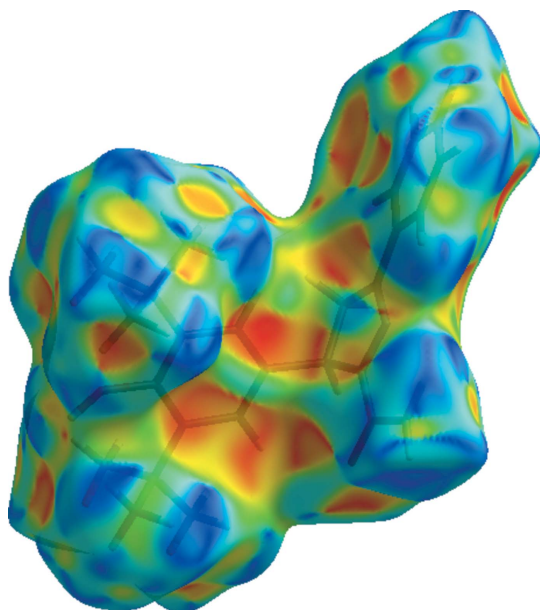


Figure 3
View of the three-dimensional Hirshfeld surface of the title compound mapped over *d*_{norm}, in the range –0.5426 to 1.7721 a.u.

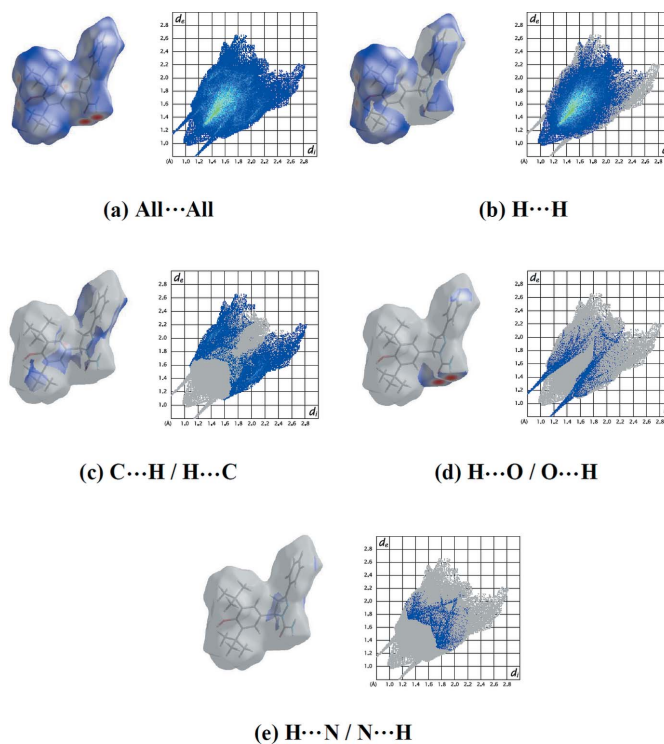

Figure 4

View of the three-dimensional Hirshfeld surface of the title compound mapped over the electrostatic potential energy in the range -0.0500 to 0.0500 a.u. using the STO-3G 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.

triangles then there are no π – π interactions. Fig. 5 clearly indicates that there are no π – π interactions present in the the crystal of the title compound, as also indicated by the analysis of the crystal structure using *PLATON* (Spek, 2009). Fig. 6*a* shows the two-dimensional fingerprint of the sum of the contacts contributing to the Hirshfeld surface represented in


Figure 5

Hirshfeld surface of the title compound mapped over the shape-index.


Figure 6

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

normal mode. These represent both the overall two-dimensional fingerprint plot and those delineated into $H \cdots H$ (68.6%), $C \cdots H/H \cdots C$ (18.3%), $H \cdots O/O \cdots H$ (7.1%) and $H \cdots N/N \cdots H$ (4.1%) contacts (Fig. 6*b–e*). The most significant contribution to the Hirshfeld surface is from $H \cdots H$ contacts (68.6%; Fig. 5*b*).

The large number of $H \cdots H$, $C \cdots H/H \cdots C$, $H \cdots O/O \cdots H$ and $H \cdots N/N \cdots H$ contacts suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

4. Synthesis and crystallization

To a solution of of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-phenylprop-2-en-1-one (1.2 mmol) in 10 ml ethanol was added semicarbazide hydrochloride (1.26 mmol). The mixture was refluxed for 3 h and then cooled to room temperature. The title compound, that precipitated as colourless single crystals, was collected by filtration and washed with an ethanol–water (1:1) mixture (yield 56%, m.p. 525 K). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 1.38 (*s*, 18H, 6 CH_3); 3.05 (*dd*, 1H, CH_2 , $^3J_{\text{H-H}} = 4.8$, $^2J_{\text{H-H}} = 17.7$); 3.75 (*dd*, 1H, CH_2 , $^3J_{\text{H-H}} = 12$, $^2J_{\text{H-H}} = 17.7$); 5.35 (*dd*, 1H, CH_2 , $^3J_{\text{H-H}} = 4.8$, $^2J_{\text{H-H}} = 11.7$); 6.51 (*s*, 2H, NH_2); 6.87 (*s*, 1H, OH_{ar}); 6.96 (*s*, 2H, 2 Ar-H); 7.41–7.83 (*m*, 5H, 5 Ar-H). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): 30.79 (6 CH_3), 34.94 (2 C_{tert}), 43.00 (CH_2), 60.32 (CH), 121.79 (2 CH_{ar}), 126.90 (2 CH_{ar}), 129.39 (2 CH_{ar}), 130.02 (CH_{ar}), 132.18 (C_{ar}), 134.96

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₄ H ₃₁ N ₃ O ₂
<i>M_r</i>	393.52
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.095 (3), 10.215 (4), 17.995 (8)
α , β , γ (°)	84.781 (15), 85.688 (15), 76.012 (15)
<i>V</i> (Å ³)	1081.1 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.08
Crystal size (mm)	0.20 × 0.16 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2003)
<i>T</i> _{min} , <i>T</i> _{max}	0.976, 0.982
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	27614, 5128, 3573
<i>R</i> _{int}	0.093
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.659
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.055, 0.163, 1.03
No. of reflections	5128
No. of parameters	278
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.34, -0.20

Computer programs: *APEX2* and *SAINT* (Bruker, 2003), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(C_{ar}), 139.67 (C_{ar}), 151.13(N=C_{tert}), 153.23 (O—C_{ar}) 155.56 (NC=O).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms of the amino group were located in a difference-Fourier map and refined freely. The hydroxy H atom (H15) was included in the calculated position (AFIX 147; O—H = 0.84 Å) and refined with *U*_{iso}(H) = 1.5*U*_{eq}(O). All the C-bound H atoms were placed in calculated positions and refined using a riding model: C—H = 0.95–1.00 Å with *U*_{iso}(H) = 1.2*U*_{eq}(C).

As reported previously (*cf.* Cambridge Structural Database; Groom *et al.*, 2016) short H...H contacts (< 2.0 Å), involving the hydroxy H atom and the methyl H atoms of the 3,5-di-*tert*-butyl-4-hydroxyphenyl moiety, were observed.

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supporting information

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Crystal structure and Hirshfeld surface analysis of 5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide

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Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009).

5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide

Crystal data

$C_{24}H_{31}N_3O_2$	$Z = 2$
$M_r = 393.52$	$F(000) = 424$
Triclinic, $P\bar{1}$	$D_x = 1.209 \text{ Mg m}^{-3}$
$a = 6.095 (3) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 10.215 (4) \text{ \AA}$	Cell parameters from 7006 reflections
$c = 17.995 (8) \text{ \AA}$	$\theta = 2.3\text{--}27.5^\circ$
$\alpha = 84.781 (15)^\circ$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 85.688 (15)^\circ$	$T = 150 \text{ K}$
$\gamma = 76.012 (15)^\circ$	Plate, colorless
$V = 1081.1 (8) \text{ \AA}^3$	$0.20 \times 0.16 \times 0.13 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	5128 independent reflections
φ and ω scans	3573 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$R_{\text{int}} = 0.093$
$T_{\text{min}} = 0.976$, $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
27614 measured reflections	$h = -8 \rightarrow 8$
	$k = -13 \rightarrow 13$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.055$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.163$	$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.1168P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
5128 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
278 parameters	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
Primary atom site location: dual	

Extinction correction: (SHELXL-2018/3;
Sheldrick, 2015b),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.045 (10)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O15	0.9461 (2)	0.44716 (13)	0.91734 (7)	0.0566 (4)
H15	1.033732	0.369748	0.919753	0.085*
O29	0.8119 (2)	0.43979 (12)	0.57125 (7)	0.0481 (3)
N19	0.3611 (2)	0.72589 (13)	0.58893 (7)	0.0346 (3)
N20	0.5033 (2)	0.59925 (13)	0.60307 (7)	0.0370 (3)
N28	0.7453 (3)	0.64582 (18)	0.50555 (9)	0.0523 (4)
H28A	0.882 (4)	0.625 (2)	0.4835 (13)	0.067 (7)*
H28B	0.659 (4)	0.732 (2)	0.5038 (12)	0.063 (6)*
C1	0.8395 (2)	0.35284 (15)	0.81126 (8)	0.0317 (3)
C2	0.8169 (3)	0.46205 (15)	0.85614 (8)	0.0344 (3)
C3	0.6665 (2)	0.58842 (15)	0.84134 (8)	0.0314 (3)
C4	0.5350 (2)	0.60223 (15)	0.77960 (8)	0.0313 (3)
H4	0.429397	0.685704	0.768849	0.038*
C5	0.5536 (2)	0.49774 (14)	0.73326 (8)	0.0293 (3)
C6	0.7058 (2)	0.37542 (15)	0.74962 (8)	0.0314 (3)
H6	0.719460	0.304401	0.717703	0.038*
C7	1.0061 (3)	0.21512 (15)	0.82845 (9)	0.0355 (4)
C8	0.9502 (4)	0.1510 (2)	0.90606 (11)	0.0568 (5)
H8A	0.795804	0.137693	0.908130	0.085*
H8B	0.961692	0.210912	0.944383	0.085*
H8C	1.057342	0.063409	0.915125	0.085*
C9	0.9923 (4)	0.11345 (18)	0.77254 (12)	0.0586 (6)
H9A	0.838694	0.098943	0.775293	0.088*
H9B	1.100388	0.027416	0.784629	0.088*
H9C	1.029174	0.148899	0.721901	0.088*
C10	1.2512 (3)	0.2323 (2)	0.82225 (13)	0.0581 (5)
H10A	1.354990	0.145275	0.835704	0.087*
H10B	1.265658	0.298983	0.856270	0.087*
H10C	1.288924	0.263391	0.770813	0.087*
C11	0.6506 (3)	0.70679 (16)	0.89082 (9)	0.0368 (4)
C12	0.8800 (3)	0.7458 (2)	0.88750 (12)	0.0533 (5)
H12A	0.924088	0.769747	0.835484	0.080*
H12B	0.995181	0.669096	0.907726	0.080*
H12C	0.866678	0.823474	0.917172	0.080*
C13	0.4760 (3)	0.83347 (17)	0.86389 (11)	0.0509 (5)

H13A	0.519650	0.862799	0.812705	0.076*
H13B	0.469798	0.905832	0.896767	0.076*
H13C	0.326834	0.812938	0.864961	0.076*
C14	0.5774 (4)	0.6689 (2)	0.97178 (10)	0.0533 (5)
H14A	0.569824	0.744823	1.002283	0.080*
H14B	0.687629	0.589255	0.991622	0.080*
H14C	0.427997	0.648596	0.973155	0.080*
C16	0.4155 (2)	0.51573 (15)	0.66436 (8)	0.0318 (3)
H16	0.417377	0.425207	0.646982	0.038*
C17	0.1694 (3)	0.59885 (16)	0.67369 (9)	0.0358 (4)
H17A	0.062980	0.553619	0.653335	0.043*
H17B	0.124746	0.613620	0.726873	0.043*
C18	0.1762 (3)	0.73077 (15)	0.62880 (8)	0.0318 (3)
C21	-0.0090 (3)	0.85374 (15)	0.62682 (8)	0.0339 (3)
C22	-0.2214 (3)	0.84869 (19)	0.65965 (10)	0.0443 (4)
H22	-0.244531	0.766713	0.684641	0.053*
C23	-0.3989 (3)	0.9624 (2)	0.65606 (11)	0.0540 (5)
H23	-0.543486	0.957730	0.678261	0.065*
C24	-0.3679 (4)	1.0824 (2)	0.62059 (11)	0.0559 (5)
H24	-0.490868	1.159998	0.618221	0.067*
C25	-0.1580 (4)	1.08977 (18)	0.58852 (10)	0.0526 (5)
H25	-0.136101	1.172570	0.564262	0.063*
C26	0.0211 (3)	0.97629 (17)	0.59169 (9)	0.0421 (4)
H26	0.165500	0.981990	0.569754	0.050*
C27	0.6958 (3)	0.55571 (17)	0.55953 (8)	0.0364 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O15	0.0598 (8)	0.0483 (8)	0.0558 (8)	0.0115 (6)	-0.0335 (7)	-0.0142 (6)
O29	0.0416 (7)	0.0390 (7)	0.0552 (7)	0.0044 (5)	0.0052 (5)	-0.0021 (5)
N19	0.0345 (7)	0.0325 (7)	0.0321 (6)	0.0012 (5)	-0.0051 (5)	0.0004 (5)
N20	0.0347 (7)	0.0341 (7)	0.0346 (7)	0.0038 (6)	-0.0014 (5)	0.0040 (5)
N28	0.0468 (9)	0.0471 (9)	0.0509 (9)	0.0039 (7)	0.0122 (7)	0.0060 (7)
C1	0.0278 (7)	0.0277 (7)	0.0364 (8)	0.0002 (6)	-0.0051 (6)	-0.0013 (6)
C2	0.0324 (8)	0.0331 (8)	0.0357 (8)	-0.0012 (6)	-0.0106 (6)	-0.0023 (6)
C3	0.0300 (7)	0.0275 (7)	0.0356 (7)	-0.0042 (6)	-0.0035 (6)	-0.0029 (6)
C4	0.0288 (7)	0.0253 (7)	0.0371 (7)	-0.0013 (6)	-0.0056 (6)	0.0009 (5)
C5	0.0271 (7)	0.0280 (7)	0.0316 (7)	-0.0045 (6)	-0.0037 (6)	0.0006 (5)
C6	0.0307 (7)	0.0279 (7)	0.0342 (7)	-0.0031 (6)	-0.0043 (6)	-0.0036 (6)
C7	0.0319 (8)	0.0293 (8)	0.0403 (8)	0.0038 (6)	-0.0082 (6)	-0.0012 (6)
C8	0.0649 (13)	0.0419 (10)	0.0526 (11)	0.0039 (9)	-0.0012 (9)	0.0082 (8)
C9	0.0647 (12)	0.0359 (9)	0.0659 (12)	0.0164 (9)	-0.0251 (10)	-0.0144 (8)
C10	0.0343 (9)	0.0522 (11)	0.0808 (14)	0.0033 (8)	-0.0065 (9)	-0.0010 (10)
C11	0.0372 (8)	0.0305 (8)	0.0420 (8)	-0.0035 (6)	-0.0070 (7)	-0.0073 (6)
C12	0.0489 (11)	0.0490 (11)	0.0676 (12)	-0.0172 (9)	-0.0082 (9)	-0.0148 (9)
C13	0.0564 (11)	0.0323 (9)	0.0596 (11)	0.0044 (8)	-0.0117 (9)	-0.0130 (8)
C14	0.0617 (12)	0.0520 (11)	0.0436 (10)	-0.0063 (10)	0.0000 (9)	-0.0113 (8)

C16	0.0302 (7)	0.0288 (7)	0.0350 (7)	-0.0033 (6)	-0.0073 (6)	0.0002 (6)
C17	0.0290 (8)	0.0358 (8)	0.0409 (8)	-0.0043 (6)	-0.0092 (6)	0.0025 (6)
C18	0.0311 (7)	0.0335 (8)	0.0296 (7)	-0.0028 (6)	-0.0078 (6)	-0.0028 (6)
C21	0.0353 (8)	0.0339 (8)	0.0298 (7)	-0.0003 (6)	-0.0085 (6)	-0.0045 (6)
C22	0.0351 (9)	0.0435 (10)	0.0512 (10)	-0.0024 (7)	-0.0059 (7)	-0.0036 (7)
C23	0.0362 (9)	0.0607 (12)	0.0585 (11)	0.0057 (8)	-0.0069 (8)	-0.0123 (9)
C24	0.0552 (12)	0.0488 (11)	0.0515 (11)	0.0191 (9)	-0.0180 (9)	-0.0130 (8)
C25	0.0709 (13)	0.0349 (9)	0.0442 (9)	0.0049 (9)	-0.0136 (9)	-0.0006 (7)
C26	0.0491 (10)	0.0379 (9)	0.0354 (8)	-0.0022 (7)	-0.0059 (7)	-0.0016 (6)
C27	0.0326 (8)	0.0388 (8)	0.0345 (8)	-0.0009 (7)	-0.0029 (6)	-0.0048 (6)

Geometric parameters (Å, °)

O15—C2	1.3776 (19)	C10—H10B	0.9800
O15—H15	0.8400	C10—H10C	0.9800
O29—C27	1.233 (2)	C11—C13	1.529 (2)
N19—C18	1.282 (2)	C11—C14	1.534 (3)
N19—N20	1.3859 (18)	C11—C12	1.539 (3)
N20—C27	1.364 (2)	C12—H12A	0.9800
N20—C16	1.480 (2)	C12—H12B	0.9800
N28—C27	1.345 (2)	C12—H12C	0.9800
N28—H28A	0.88 (3)	C13—H13A	0.9800
N28—H28B	0.91 (2)	C13—H13B	0.9800
C1—C6	1.395 (2)	C13—H13C	0.9800
C1—C2	1.410 (2)	C14—H14A	0.9800
C1—C7	1.544 (2)	C14—H14B	0.9800
C2—C3	1.407 (2)	C14—H14C	0.9800
C3—C4	1.395 (2)	C16—C17	1.540 (2)
C3—C11	1.546 (2)	C16—H16	1.0000
C4—C5	1.392 (2)	C17—C18	1.515 (2)
C4—H4	0.9500	C17—H17A	0.9900
C5—C6	1.386 (2)	C17—H17B	0.9900
C5—C16	1.523 (2)	C18—C21	1.472 (2)
C6—H6	0.9500	C21—C22	1.393 (2)
C7—C9	1.531 (2)	C21—C26	1.397 (2)
C7—C8	1.538 (3)	C22—C23	1.383 (2)
C7—C10	1.541 (3)	C22—H22	0.9500
C8—H8A	0.9800	C23—C24	1.377 (3)
C8—H8B	0.9800	C23—H23	0.9500
C8—H8C	0.9800	C24—C25	1.380 (3)
C9—H9A	0.9800	C24—H24	0.9500
C9—H9B	0.9800	C25—C26	1.387 (2)
C9—H9C	0.9800	C25—H25	0.9500
C10—H10A	0.9800	C26—H26	0.9500
C2—O15—H15	109.5	C12—C11—C3	109.96 (13)
C18—N19—N20	108.15 (13)	C11—C12—H12A	109.5
C27—N20—N19	121.43 (13)	C11—C12—H12B	109.5

C27—N20—C16	124.77 (13)	H12A—C12—H12B	109.5
N19—N20—C16	113.61 (12)	C11—C12—H12C	109.5
C27—N28—H28A	116.5 (15)	H12A—C12—H12C	109.5
C27—N28—H28B	118.7 (14)	H12B—C12—H12C	109.5
H28A—N28—H28B	122 (2)	C11—C13—H13A	109.5
C6—C1—C2	116.81 (13)	C11—C13—H13B	109.5
C6—C1—C7	121.23 (13)	H13A—C13—H13B	109.5
C2—C1—C7	121.95 (13)	C11—C13—H13C	109.5
O15—C2—C3	117.36 (13)	H13A—C13—H13C	109.5
O15—C2—C1	119.80 (13)	H13B—C13—H13C	109.5
C3—C2—C1	122.84 (13)	C11—C14—H14A	109.5
C4—C3—C2	116.96 (13)	C11—C14—H14B	109.5
C4—C3—C11	121.73 (13)	H14A—C14—H14B	109.5
C2—C3—C11	121.31 (13)	C11—C14—H14C	109.5
C5—C4—C3	122.16 (13)	H14A—C14—H14C	109.5
C5—C4—H4	118.9	H14B—C14—H14C	109.5
C3—C4—H4	118.9	N20—C16—C5	111.58 (12)
C6—C5—C4	118.82 (13)	N20—C16—C17	100.20 (11)
C6—C5—C16	119.48 (13)	C5—C16—C17	115.44 (13)
C4—C5—C16	121.69 (13)	N20—C16—H16	109.7
C5—C6—C1	122.39 (14)	C5—C16—H16	109.7
C5—C6—H6	118.8	C17—C16—H16	109.7
C1—C6—H6	118.8	C18—C17—C16	102.79 (13)
C9—C7—C8	106.08 (16)	C18—C17—H17A	111.2
C9—C7—C10	107.04 (16)	C16—C17—H17A	111.2
C8—C7—C10	110.82 (15)	C18—C17—H17B	111.2
C9—C7—C1	111.32 (13)	C16—C17—H17B	111.2
C8—C7—C1	111.35 (13)	H17A—C17—H17B	109.1
C10—C7—C1	110.08 (14)	N19—C18—C21	121.19 (14)
C7—C8—H8A	109.5	N19—C18—C17	113.38 (13)
C7—C8—H8B	109.5	C21—C18—C17	125.40 (14)
H8A—C8—H8B	109.5	C22—C21—C26	118.56 (15)
C7—C8—H8C	109.5	C22—C21—C18	119.78 (15)
H8A—C8—H8C	109.5	C26—C21—C18	121.66 (15)
H8B—C8—H8C	109.5	C23—C22—C21	120.35 (18)
C7—C9—H9A	109.5	C23—C22—H22	119.8
C7—C9—H9B	109.5	C21—C22—H22	119.8
H9A—C9—H9B	109.5	C24—C23—C22	120.60 (19)
C7—C9—H9C	109.5	C24—C23—H23	119.7
H9A—C9—H9C	109.5	C22—C23—H23	119.7
H9B—C9—H9C	109.5	C23—C24—C25	119.85 (17)
C7—C10—H10A	109.5	C23—C24—H24	120.1
C7—C10—H10B	109.5	C25—C24—H24	120.1
H10A—C10—H10B	109.5	C24—C25—C26	120.03 (18)
C7—C10—H10C	109.5	C24—C25—H25	120.0
H10A—C10—H10C	109.5	C26—C25—H25	120.0
H10B—C10—H10C	109.5	C25—C26—C21	120.60 (18)
C13—C11—C14	106.92 (15)	C25—C26—H26	119.7

C13—C11—C12	106.76 (15)	C21—C26—H26	119.7
C14—C11—C12	110.53 (15)	O29—C27—N28	124.31 (15)
C13—C11—C3	111.83 (13)	O29—C27—N20	119.69 (15)
C14—C11—C3	110.74 (14)	N28—C27—N20	116.00 (15)
C18—N19—N20—C27	168.45 (14)	C27—N20—C16—C5	74.87 (19)
C18—N19—N20—C16	-6.82 (17)	N19—N20—C16—C5	-110.05 (14)
C6—C1—C2—O15	-179.18 (15)	C27—N20—C16—C17	-162.42 (14)
C7—C1—C2—O15	0.0 (2)	N19—N20—C16—C17	12.66 (16)
C6—C1—C2—C3	0.6 (2)	C6—C5—C16—N20	-104.30 (16)
C7—C1—C2—C3	179.85 (14)	C4—C5—C16—N20	74.21 (18)
O15—C2—C3—C4	-179.49 (14)	C6—C5—C16—C17	142.19 (14)
C1—C2—C3—C4	0.7 (2)	C4—C5—C16—C17	-39.3 (2)
O15—C2—C3—C11	1.3 (2)	N20—C16—C17—C18	-12.66 (14)
C1—C2—C3—C11	-178.56 (15)	C5—C16—C17—C18	107.30 (14)
C2—C3—C4—C5	-1.4 (2)	N20—N19—C18—C21	179.27 (12)
C11—C3—C4—C5	177.80 (14)	N20—N19—C18—C17	-2.84 (17)
C3—C4—C5—C6	0.8 (2)	C16—C17—C18—N19	10.54 (16)
C3—C4—C5—C16	-177.68 (14)	C16—C17—C18—C21	-171.67 (13)
C4—C5—C6—C1	0.6 (2)	N19—C18—C21—C22	168.31 (14)
C16—C5—C6—C1	179.16 (14)	C17—C18—C21—C22	-9.3 (2)
C2—C1—C6—C5	-1.3 (2)	N19—C18—C21—C26	-10.7 (2)
C7—C1—C6—C5	179.48 (14)	C17—C18—C21—C26	171.63 (14)
C6—C1—C7—C9	-2.4 (2)	C26—C21—C22—C23	1.2 (2)
C2—C1—C7—C9	178.43 (16)	C18—C21—C22—C23	-177.89 (15)
C6—C1—C7—C8	-120.56 (17)	C21—C22—C23—C24	-0.5 (3)
C2—C1—C7—C8	60.3 (2)	C22—C23—C24—C25	-0.2 (3)
C6—C1—C7—C10	116.12 (17)	C23—C24—C25—C26	0.3 (3)
C2—C1—C7—C10	-63.0 (2)	C24—C25—C26—C21	0.3 (3)
C4—C3—C11—C13	0.8 (2)	C22—C21—C26—C25	-1.1 (2)
C2—C3—C11—C13	180.00 (15)	C18—C21—C26—C25	177.97 (14)
C4—C3—C11—C14	119.93 (17)	N19—N20—C27—O29	-176.12 (14)
C2—C3—C11—C14	-60.9 (2)	C16—N20—C27—O29	-1.4 (2)
C4—C3—C11—C12	-117.62 (17)	N19—N20—C27—N28	4.0 (2)
C2—C3—C11—C12	61.6 (2)	C16—N20—C27—N28	178.67 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N28—H28 <i>B</i> ...N19	0.91 (2)	2.30 (2)	2.678 (3)	105 (2)
N28—H28 <i>A</i> ...O29 ⁱ	0.88 (2)	2.03 (2)	2.912 (3)	174 (2)

Symmetry code: (i) $-x+2, -y+1, -z+1$.