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Synthesis and crystal structure of 1-hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde

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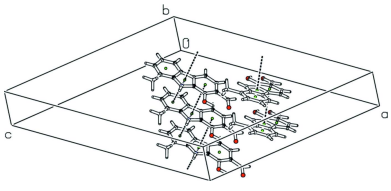
Two crystallographically independent molecules are present in the asymmetric unit of the title compound, $C_{14}H_{11}NO_2$, with virtually identical geometries. The carbazole units are planar. The hydroxy group at position 1, carbaldehyde group at position 2, and methyl group at position 8 (with the exception of two H atoms) are coplanar with the attached benzene rings. The dihedral angle between the two benzene rings is 2.20 (9)° in molecule *A* and 2.01 (9)° in molecule *B*. The pyrrole ring makes dihedral angles of 0.82 (10) and 1.40 (10)° [0.84 (10) and 1.18 (10)° in molecule *B*] with the (–CH_3)-substituted and (–OH and –CHO) substituted benzene rings, respectively. The molecular structure is stabilized by the intramolecular O—H···O hydrogen bonds, while the crystal structure features N—H···O and C—H···O hydrogen bonds. A range of π–π contacts further stabilizes the crystal structure.

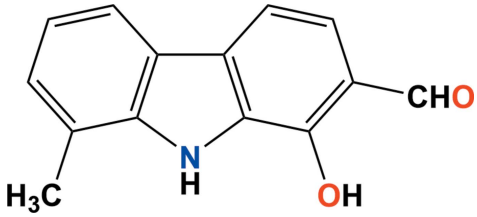
1. Chemical context

Nitrogen-containing heterocyclic compounds are key building blocks used to develop chemicals of biological and medicinal interest. Among nitrogen heterocycles, carbazole alkaloids represent an important class of natural products. The Indian medicinal plant *Murraya koenigii spreng* (Rutaceae) is a rich source of carbazole alkaloids (Knölker & Reddy, 2002), and a number of these natural products with novel structures and useful biological activities have been isolated from this plant over the past decades. The increase of isolable natural products as well as the pharmacological action of these carbazole derivatives has generated synthetic interest; consequently, the synthesis of carbazoles has been an active area of study.

Based on the structural, biological and pharmacological importance of carbazole derivatives, the present investigation was to devise a viable synthetic route to these compounds using different methodologies. For our synthetic strategy, 2,3,4,9-tetrahydro-1*H*-carbazol-1-ones prepared in our laboratory were used as precursors, opening new avenues for the synthesis of highly functionalized carbazole derivatives such as 1-hydroxyimino-2,3,4,9-tetrahydro-1*H*-carbazoles, 1-hydroxycarbazoles, and 1-hydroxy-2-formylcarbazoles. The functionalized carbazoles thus prepared lead to mukonine isomers, oxazolocarbazoles, girinimbine isomers, pyranocarbazoles, indoloisoflavones, indolocoumarins, indoloxanthones, benzocarbazoles, carbazolyloxypropanolamines and pyrazolo-, isoxazolo-, furo-, oxazino-, pyrimido-, pyridazino-,



pyrido-, pyrazino- and indolo-carbazoles in excellent yields (Shanmugasundaram & Rajendra Prasad, 1999; Sridharan & Rajendra Prasad, 2011; Sridharan, Beagle *et al.*, 2008 and references cited therein). Herein, we report the synthesis and crystal structure of 1-hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde (Fig. 1), which is a potential precursor for the synthesis of many hetero-annulated carbazoles (Gunaseelan *et al.*, 2007).



2. Structural commentary

The title compound crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules (*A* and *B*, Fig. 1) in the asymmetric unit. They are superimposable and both are essentially planar. Placing inverted molecule *B* on molecule *A* gives the best fit, with the overlay of the two independent molecules shown in Fig. 2. The weighted r.m.s. fit of the 17 non-H fitted atoms is 0.034 Å, the r.m.s. bond fit is 0.003 Å and the r.m.s. angle fit is 0.383°. Both independent molecules, including the hydroxy group at position 1, carbaldehyde group at position 2, and methyl group at position 8 (with the exception of two H atoms) are near planar. The dihedral angle between the two benzene rings of the carbazole is 2.20 (9)° in molecule *A* and 2.01 (9)° in molecule *B*. The pyrrole ring makes dihedral angles of 0.82 (10) and 1.40 (10)° for molecule *A* and 0.84 (10) and 1.18 (10)° for molecule *B* with the methyl-substituted and hydroxide/carbaldehyde-substituted benzene rings, respectively. The compound exhibits intramolecular O—H···O hydrogen bonding between the hydroxide and aldehyde groups (Table 1). Hydrogen bonds similar to the O1—H1*D*···O2 and O3—H3*A*···O4 bonds observed in this structure, forming *S*(6) ring motifs, have previously been observed (Bernstein *et al.*, 1995).

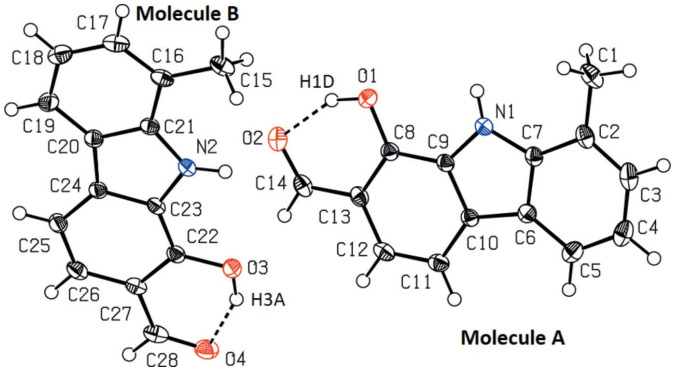


Figure 1
The two crystallographically independent molecules with the atom-numbering scheme. Non-H atoms are shown at the 50% displacement ellipsoid probability level, H atoms are represented as small spheres.

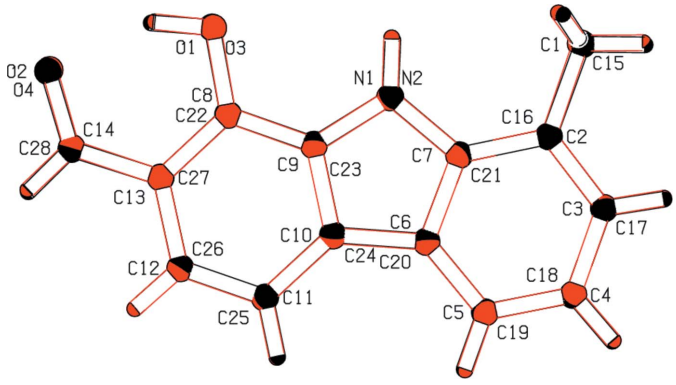


Figure 2
Least-squares overlay of the two independent molecules (inverted molecule *B* on molecule *A*). Fit rotation angle is −172.76°, r.m.s. fit = 0.087 Å.

3. Supramolecular features

In the crystal, molecules are connected into chains parallel to the *c* axis by intermolecular N—H···O and C—H···O hydrogen bonds (Table 1, Fig. 3). Both crystallographically independent molecules are arranged in similar N1—

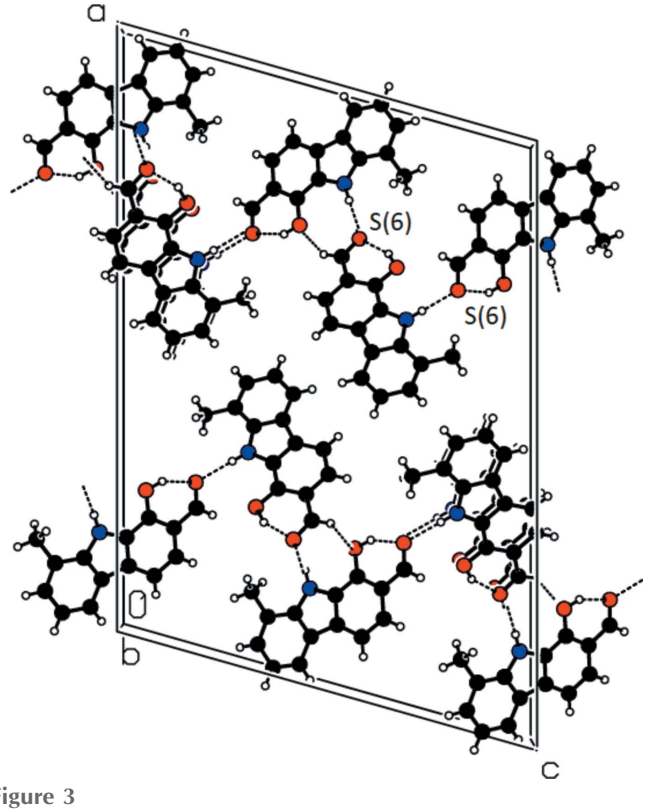


Figure 3
Perspective partial packing view of the title compound, viewed along the *b* axis, showing the hydrogen-bonding interactions. Black dashed lines indicate the N—H···O, O—H···O and C—H···O hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O3^{i}	0.93	2.50	3.254 (2)	138
N1—H1···O4^{ii}	0.87 (2)	2.00 (2)	2.862 (2)	174 (2)
O1—H1D···O2	0.94 (3)	1.74 (3)	2.602 (2)	151 (3)
N2—H2···O2^{iii}	0.91 (2)	1.97 (2)	2.879 (2)	173 (2)
O3—H3A···O4	0.90 (3)	1.78 (3)	2.595 (2)	150 (3)

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

H1···O4(x, $\frac{1}{2}-y$, $\frac{1}{2}+z$) and N2—H2···O2(x, $1+y$, z) hydrogen bonds. A C14—H14···O3(x, $-1+y$, z) hydrogen bond is also present. A range of π–π contacts is also observed (Fig. 4). The distances between ring centroids are $Cg1\cdots Cg2(x, -1+y, z)$ = 3.4604 (13) Å, $Cg1\cdots Cg3$ (x, $1+y$, z) = 3.4896 (13) Å and $Cg7\cdots Cg9$ (x, $1+y$, z) = 3.6279 (13) Å, where $Cg1$, $Cg2$, $Cg3$, $Cg7$ and $Cg9$ are the centroids of the N1/C7/C6/C10/C9, C2–C7, C8–C13, N2/C21/C20/C24/C23 and C22–C27 rings, respectively.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.42, update May 2021; Groom *et al.*, 2016) for the structure 1-hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde gave two hits, *viz*. 2,2,10-trimethyl-2,3-dihydropyrano(2,3-a)carbazol-4(11*H*)-one (CSD refcode: BOGTOH; Sridharan, Prasad *et al.*, 2008) and 1-(1-hydroxy-8-methyl-9*H*-carbazol-2-yl)ethanone (CSD refcode: WACYEG; Archana *et al.*, 2010). A search for the structure of 9*H*-carbazole-1-ol gave 69 hits. 1-Hydroxy-3-methyl-9*H*-carbazole-2-carbaldehyde, $C_{14}H_{11}NO_2$, (CSD refcode: NIFCUB; Gunaseelan *et al.*, 2007) has the most similar structure to that of the title compound, with a 3-methyl rather than an 8-methyl group. The structure of NIFCUB is similarly stabilized by inter- and intramolecular N—H···O and O—H···O hydrogen bonds.

5. Synthesis and crystallization

30% Sodium hydride in mineral oil (2.4 g) was washed with dry benzene and taken into a round-bottom flask containing dry benzene (100 ml). The flask was kept in an ice bath under stirring. Ethyl formate (8 ml) was added dropwise to the solution over a period of 10 minutes. Then 8-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one (1.6 g, 0.008 mol) in dry benzene (25 ml) was added slowly and the reaction mixture was allowed to stir for another 36 h. The reaction was monitored by TLC. After completion of the reaction, benzene was removed *in vacuo* and the contents in the flask were transferred to a beaker containing water. It was neutralized with dilute HCl, filtered, washed with water and dried to get crude 1-hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde. It was purified by column chromatography over silica using petroleum ether:ethyl acetate (95:5) as eluant. The brown pure product obtained was recrystallized using glacial acetic acid (needle-shaped crystals, yield 0.965 g, 55%), m.p. 414 K (Fig. 5).

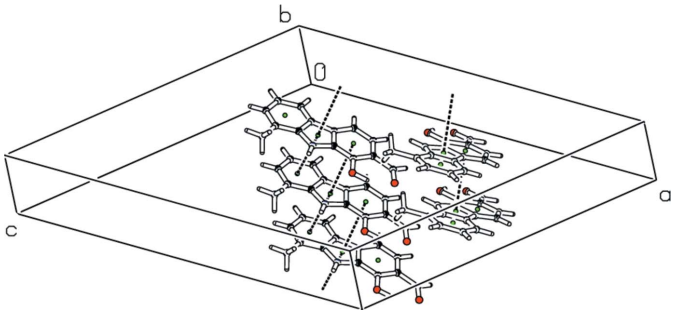


Figure 4
Straw-style packing view of the title compound, viewed down the *b* axis, showing slipped π–π stacking interactions. Centroids are indicated by green spheres and contacts between centroids by black dotted lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{11}NO_2$
M_r	225.24
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	28.290 (5), 3.9052 (7), 20.264 (3)
β (°)	105.817 (2)
V (Å^3)	2154.0 (6)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.75 × 0.19 × 0.10
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.830, 0.991
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19760, 5344, 4453
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.146, 1.18
No. of reflections	5344
No. of parameters	325
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXTL* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The indole NH hydrogen atoms,

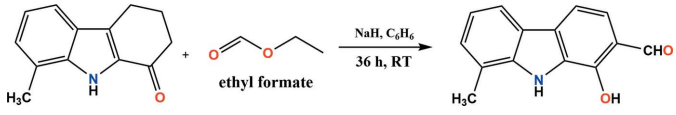


Figure 5
Synthesis of the title compound.

H1 and H2 and the hydroxyl OH hydrogen atoms H1*D* and H3*A* were located in a difference-Fourier map and freely refined. The remaining hydrogen atoms were placed in calculated positions with C—H bond distances of 0.93 Å (aromatic H), or 0.96 Å (methyl H) and were refined with anisotropic displacement parameters 1.2 and 1.5 times that of the parent carbon atoms.

Acknowledgements

AAT remembers the long time association and research collaboration with the late Professor Jerry P. Jasinski of the Department of Chemistry, Keene State College, USA. MS thanks the academic and administrative authorities of RV College of Engineering for their support and encouragement.

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supporting information

Acta Cryst. (2021). E**77**, 867-870 [https://doi.org/10.1107/S2056989021007210]

Synthesis and crystal structure of 1-hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde

Aravazhi Amalan Thiruvalluvar, M. Sridharan, K. J. Rajendra Prasad and M. Zeller

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

1-Hydroxy-8-methyl-9*H*-carbazole-2-carbaldehyde

Crystal data

$C_{14}H_{11}NO_2$
M_r = 225.24
Monoclinic, $P2_1/c$
a = 28.290 (5) Å
b = 3.9052 (7) Å
c = 20.264 (3) Å
β = 105.817 (2)°
V = 2154.0 (6) Å^3
Z = 8
$F(000)$ = 944
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7327 reflections
θ = 2.2–31.3°
μ = 0.09 mm^{-1}
T = 296 K
Needle, brown
0.75 × 0.19 × 0.10 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2005)
T_{min} = 0.830, T_{max} = 0.991
19760 measured reflections
5344 independent reflections
4453 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 28.3°, θ_{min} = 1.5°
h = −37→37
k = −5→5
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.146
S = 1.18
5344 reflections
325 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 1.1713P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.60695 (8)	0.8782 (6)	0.79934 (10)	0.0305 (4)
H1A	0.586381	0.993978	0.822872	0.046*
H1B	0.636607	1.007032	0.804205	0.046*
H1C	0.614950	0.654265	0.818701	0.046*
C2	0.58026 (7)	0.8460 (5)	0.72475 (10)	0.0225 (4)
C3	0.53306 (7)	0.9707 (5)	0.69748 (11)	0.0269 (4)
H3	0.517561	1.081062	0.726518	0.032*
C4	0.50767 (7)	0.9371 (5)	0.62778 (11)	0.0278 (4)
H4	0.475869	1.021909	0.611961	0.033*
C5	0.52935 (6)	0.7800 (5)	0.58267 (10)	0.0239 (4)
H5	0.512575	0.758554	0.536525	0.029*
C6	0.57725 (6)	0.6531 (5)	0.60773 (9)	0.0190 (3)
C7	0.60179 (6)	0.6862 (5)	0.67805 (9)	0.0187 (3)
C8	0.69229 (6)	0.2303 (5)	0.61767 (9)	0.0186 (3)
C9	0.65285 (6)	0.4087 (4)	0.62986 (8)	0.0171 (3)
C10	0.61009 (6)	0.4752 (5)	0.57646 (8)	0.0173 (3)
C11	0.60642 (6)	0.3678 (5)	0.50886 (9)	0.0213 (4)
H11	0.578573	0.416290	0.473378	0.026*
C12	0.64511 (7)	0.1896 (5)	0.49680 (9)	0.0213 (4)
H12	0.643093	0.114554	0.452561	0.026*
C13	0.68800 (6)	0.1176 (5)	0.55022 (9)	0.0199 (4)
C14	0.72687 (7)	−0.0821 (5)	0.53619 (10)	0.0230 (4)
H14	0.722444	−0.163999	0.491820	0.028*
C15	0.88208 (8)	0.8160 (5)	0.68439 (9)	0.0265 (4)
H15A	0.902174	0.905029	0.726989	0.040*
H15B	0.860603	0.642822	0.693463	0.040*
H15C	0.862872	0.997972	0.658394	0.040*
C16	0.91438 (7)	0.6628 (5)	0.64413 (9)	0.0214 (4)
C17	0.96492 (7)	0.6431 (5)	0.66858 (9)	0.0256 (4)
H17	0.979856	0.730010	0.711994	0.031*
C18	0.99471 (7)	0.4977 (5)	0.63077 (10)	0.0270 (4)
H18	1.028583	0.491116	0.649516	0.032*
C19	0.97440 (7)	0.3645 (5)	0.56619 (9)	0.0232 (4)
H19	0.994149	0.267196	0.541288	0.028*
C20	0.92328 (6)	0.3795 (5)	0.53906 (9)	0.0187 (3)
C21	0.89409 (6)	0.5292 (5)	0.57814 (8)	0.0179 (3)
C22	0.80092 (6)	0.2763 (5)	0.42718 (9)	0.0183 (3)
C23	0.84263 (6)	0.3534 (4)	0.47993 (8)	0.0176 (3)
C24	0.89000 (6)	0.2655 (5)	0.47573 (8)	0.0180 (3)

C25	0.89635 (7)	0.0985 (5)	0.41705 (9)	0.0218 (4)
H25	0.927599	0.043979	0.413640	0.026*
C26	0.85547 (7)	0.0181 (5)	0.36514 (9)	0.0232 (4)
H26	0.859196	−0.093655	0.326343	0.028*
C27	0.80755 (7)	0.1021 (5)	0.36941 (9)	0.0206 (4)
C28	0.76490 (7)	−0.0010 (5)	0.31623 (9)	0.0254 (4)
H28	0.769894	−0.116522	0.278565	0.030*
N1	0.64768 (5)	0.5391 (4)	0.69071 (8)	0.0191 (3)
N2	0.84527 (5)	0.5107 (4)	0.54173 (7)	0.0187 (3)
O1	0.73268 (5)	0.1687 (4)	0.67024 (6)	0.0238 (3)
O2	0.76604 (5)	−0.1520 (4)	0.57967 (7)	0.0276 (3)
O3	0.75629 (5)	0.3697 (4)	0.43310 (7)	0.0230 (3)
O4	0.72203 (5)	0.0536 (4)	0.31724 (7)	0.0298 (3)
H1	0.6700 (9)	0.527 (7)	0.7295 (13)	0.033 (6)*
H1D	0.7530 (11)	0.035 (9)	0.6508 (16)	0.065 (9)*
H2	0.8187 (8)	0.600 (6)	0.5531 (12)	0.031 (6)*
H3A	0.7344 (11)	0.288 (9)	0.3952 (16)	0.063 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0445 (12)	0.0266 (10)	0.0261 (10)	0.0013 (9)	0.0192 (9)	−0.0015 (8)
C2	0.0284 (9)	0.0157 (9)	0.0283 (9)	−0.0017 (7)	0.0160 (8)	0.0015 (7)
C3	0.0298 (10)	0.0167 (9)	0.0411 (11)	0.0003 (7)	0.0213 (9)	0.0011 (8)
C4	0.0212 (9)	0.0196 (9)	0.0443 (12)	0.0017 (7)	0.0120 (8)	0.0058 (8)
C5	0.0203 (8)	0.0193 (9)	0.0310 (10)	−0.0008 (7)	0.0053 (7)	0.0067 (7)
C6	0.0191 (8)	0.0169 (8)	0.0218 (8)	−0.0018 (6)	0.0068 (6)	0.0048 (7)
C7	0.0208 (8)	0.0157 (8)	0.0219 (8)	0.0002 (6)	0.0096 (7)	0.0042 (7)
C8	0.0188 (8)	0.0193 (9)	0.0182 (8)	−0.0015 (7)	0.0059 (6)	0.0015 (6)
C9	0.0181 (7)	0.0172 (8)	0.0170 (8)	−0.0028 (6)	0.0066 (6)	0.0026 (6)
C10	0.0182 (7)	0.0172 (8)	0.0173 (8)	−0.0025 (6)	0.0061 (6)	0.0034 (6)
C11	0.0227 (8)	0.0226 (9)	0.0177 (8)	−0.0034 (7)	0.0041 (6)	0.0027 (7)
C12	0.0268 (9)	0.0218 (9)	0.0158 (8)	−0.0064 (7)	0.0067 (7)	−0.0003 (7)
C13	0.0215 (8)	0.0203 (9)	0.0199 (8)	−0.0039 (7)	0.0089 (6)	−0.0004 (7)
C14	0.0276 (9)	0.0214 (9)	0.0238 (9)	−0.0023 (7)	0.0133 (7)	0.0004 (7)
C15	0.0382 (10)	0.0237 (10)	0.0179 (8)	−0.0029 (8)	0.0083 (7)	−0.0025 (7)
C16	0.0300 (9)	0.0177 (9)	0.0160 (8)	−0.0027 (7)	0.0053 (7)	0.0030 (7)
C17	0.0330 (10)	0.0216 (9)	0.0181 (8)	−0.0055 (8)	−0.0001 (7)	0.0028 (7)
C18	0.0244 (9)	0.0262 (10)	0.0265 (9)	−0.0019 (7)	0.0005 (7)	0.0064 (8)
C19	0.0226 (8)	0.0237 (10)	0.0232 (9)	0.0031 (7)	0.0062 (7)	0.0061 (7)
C20	0.0209 (8)	0.0171 (8)	0.0188 (8)	0.0008 (7)	0.0064 (6)	0.0039 (6)
C21	0.0206 (8)	0.0165 (8)	0.0166 (8)	−0.0004 (6)	0.0052 (6)	0.0034 (6)
C22	0.0214 (8)	0.0180 (8)	0.0166 (8)	0.0002 (7)	0.0068 (6)	0.0031 (6)
C23	0.0222 (8)	0.0174 (8)	0.0143 (8)	0.0004 (7)	0.0070 (6)	0.0016 (6)
C24	0.0206 (8)	0.0171 (8)	0.0171 (8)	0.0028 (6)	0.0064 (6)	0.0040 (6)
C25	0.0245 (9)	0.0225 (9)	0.0203 (8)	0.0045 (7)	0.0092 (7)	0.0024 (7)
C26	0.0325 (10)	0.0220 (9)	0.0165 (8)	0.0030 (8)	0.0093 (7)	−0.0003 (7)
C27	0.0270 (9)	0.0202 (9)	0.0143 (8)	0.0001 (7)	0.0051 (6)	0.0012 (7)

C28	0.0346 (10)	0.0233 (10)	0.0162 (8)	−0.0013 (8)	0.0035 (7)	0.0003 (7)
N1	0.0197 (7)	0.0218 (8)	0.0165 (7)	0.0019 (6)	0.0060 (6)	0.0013 (6)
N2	0.0204 (7)	0.0216 (8)	0.0149 (7)	0.0002 (6)	0.0062 (5)	−0.0005 (6)
O1	0.0187 (6)	0.0312 (8)	0.0203 (6)	0.0047 (5)	0.0034 (5)	−0.0006 (5)
O2	0.0247 (7)	0.0301 (8)	0.0308 (7)	0.0022 (6)	0.0123 (6)	−0.0014 (6)
O3	0.0186 (6)	0.0318 (8)	0.0187 (6)	−0.0013 (5)	0.0051 (5)	−0.0013 (5)
O4	0.0278 (7)	0.0397 (9)	0.0193 (6)	−0.0043 (6)	0.0019 (5)	−0.0011 (6)

Geometric parameters (Å, º)

C1—C2	1.500 (3)	C15—H15B	0.9600
C1—H1A	0.9600	C15—H15C	0.9600
C1—H1B	0.9600	C16—C17	1.382 (3)
C1—H1C	0.9600	C16—C21	1.404 (2)
C2—C3	1.387 (3)	C17—C18	1.404 (3)
C2—C7	1.404 (2)	C17—H17	0.9300
C3—C4	1.405 (3)	C18—C19	1.380 (3)
C3—H3	0.9300	C18—H18	0.9300
C4—C5	1.376 (3)	C19—C20	1.401 (2)
C4—H4	0.9300	C19—H19	0.9300
C5—C6	1.402 (2)	C20—C21	1.417 (2)
C5—H5	0.9300	C20—C24	1.440 (2)
C6—C7	1.411 (2)	C21—N2	1.379 (2)
C6—C10	1.438 (2)	C22—O3	1.350 (2)
C7—N1	1.378 (2)	C22—C23	1.392 (2)
C8—O1	1.354 (2)	C22—C27	1.410 (2)
C8—C9	1.393 (2)	C23—N2	1.379 (2)
C8—C13	1.409 (2)	C23—C24	1.408 (2)
C9—N1	1.378 (2)	C24—C25	1.410 (2)
C9—C10	1.410 (2)	C25—C26	1.371 (3)
C10—C11	1.409 (2)	C25—H25	0.9300
C11—C12	1.374 (3)	C26—C27	1.420 (3)
C11—H11	0.9300	C26—H26	0.9300
C12—C13	1.417 (2)	C27—C28	1.439 (2)
C12—H12	0.9300	C28—O4	1.237 (2)
C13—C14	1.438 (3)	C28—H28	0.9300
C14—O2	1.244 (2)	N1—H1	0.87 (2)
C14—H14	0.9300	N2—H2	0.91 (2)
C15—C16	1.505 (3)	O1—H1D	0.94 (3)
C15—H15A	0.9600	O3—H3A	0.90 (3)
C2—C1—H1A	109.5	H15A—C15—H15C	109.5
C2—C1—H1B	109.5	H15B—C15—H15C	109.5
H1A—C1—H1B	109.5	C17—C16—C21	115.81 (17)
C2—C1—H1C	109.5	C17—C16—C15	123.33 (17)
H1A—C1—H1C	109.5	C21—C16—C15	120.86 (16)
H1B—C1—H1C	109.5	C16—C17—C18	122.89 (17)
C3—C2—C7	115.79 (17)	C16—C17—H17	118.6

C3—C2—C1	122.54 (17)	C18—C17—H17	118.6
C7—C2—C1	121.68 (17)	C19—C18—C17	120.89 (18)
C2—C3—C4	122.71 (18)	C19—C18—H18	119.6
C2—C3—H3	118.6	C17—C18—H18	119.6
C4—C3—H3	118.6	C18—C19—C20	118.34 (18)
C5—C4—C3	120.74 (17)	C18—C19—H19	120.8
C5—C4—H4	119.6	C20—C19—H19	120.8
C3—C4—H4	119.6	C19—C20—C21	119.64 (16)
C4—C5—C6	118.62 (18)	C19—C20—C24	133.72 (17)
C4—C5—H5	120.7	C21—C20—C24	106.64 (15)
C6—C5—H5	120.7	N2—C21—C16	128.23 (16)
C5—C6—C7	119.64 (17)	N2—C21—C20	109.32 (15)
C5—C6—C10	133.48 (17)	C16—C21—C20	122.43 (16)
C7—C6—C10	106.86 (15)	O3—C22—C23	119.39 (15)
N1—C7—C2	128.29 (17)	O3—C22—C27	122.90 (16)
N1—C7—C6	109.21 (15)	C23—C22—C27	117.71 (16)
C2—C7—C6	122.50 (16)	N2—C23—C22	128.21 (16)
O1—C8—C9	119.60 (15)	N2—C23—C24	110.28 (15)
O1—C8—C13	122.58 (16)	C22—C23—C24	121.50 (16)
C9—C8—C13	117.81 (16)	C23—C24—C25	120.38 (16)
N1—C9—C8	128.95 (16)	C23—C24—C20	105.83 (15)
N1—C9—C10	109.92 (15)	C25—C24—C20	133.78 (16)
C8—C9—C10	121.13 (16)	C26—C25—C24	118.57 (16)
C11—C10—C9	120.79 (16)	C26—C25—H25	120.7
C11—C10—C6	133.37 (16)	C24—C25—H25	120.7
C9—C10—C6	105.84 (15)	C25—C26—C27	121.34 (17)
C12—C11—C10	118.20 (16)	C25—C26—H26	119.3
C12—C11—H11	120.9	C27—C26—H26	119.3
C10—C11—H11	120.9	C22—C27—C26	120.48 (16)
C11—C12—C13	121.50 (16)	C22—C27—C28	118.85 (17)
C11—C12—H12	119.3	C26—C27—C28	120.62 (17)
C13—C12—H12	119.3	O4—C28—C27	124.41 (18)
C8—C13—C12	120.56 (16)	O4—C28—H28	117.8
C8—C13—C14	119.52 (16)	C27—C28—H28	117.8
C12—C13—C14	119.89 (16)	C9—N1—C7	108.16 (14)
O2—C14—C13	124.09 (17)	C9—N1—H1	124.4 (16)
O2—C14—H14	118.0	C7—N1—H1	127.5 (16)
C13—C14—H14	118.0	C23—N2—C21	107.92 (15)
C16—C15—H15A	109.5	C23—N2—H2	123.7 (15)
C16—C15—H15B	109.5	C21—N2—H2	128.2 (15)
H15A—C15—H15B	109.5	C8—O1—H1D	104.5 (18)
C16—C15—H15C	109.5	C22—O3—H3A	105.7 (19)

C7—C2—C3—C4	0.8 (3)	C18—C19—C20—C21	0.0 (3)
C1—C2—C3—C4	−179.15 (19)	C18—C19—C20—C24	−178.91 (19)
C2—C3—C4—C5	−0.9 (3)	C17—C16—C21—N2	179.02 (18)
C3—C4—C5—C6	0.2 (3)	C15—C16—C21—N2	−0.9 (3)
C4—C5—C6—C7	0.5 (3)	C17—C16—C21—C20	0.7 (3)

C4—C5—C6—C10	178.98 (19)	C15—C16—C21—C20	−179.26 (17)
C3—C2—C7—N1	−179.66 (18)	C19—C20—C21—N2	−179.13 (16)
C1—C2—C7—N1	0.3 (3)	C24—C20—C21—N2	0.0 (2)
C3—C2—C7—C6	0.0 (3)	C19—C20—C21—C16	−0.5 (3)
C1—C2—C7—C6	179.92 (17)	C24—C20—C21—C16	178.64 (16)
C5—C6—C7—N1	179.06 (16)	O3—C22—C23—N2	2.3 (3)
C10—C6—C7—N1	0.2 (2)	C27—C22—C23—N2	−177.78 (17)
C5—C6—C7—C2	−0.6 (3)	O3—C22—C23—C24	−179.11 (16)
C10—C6—C7—C2	−179.45 (16)	C27—C22—C23—C24	0.8 (3)
O1—C8—C9—N1	−0.6 (3)	N2—C23—C24—C25	179.47 (16)
C13—C8—C9—N1	178.76 (17)	C22—C23—C24—C25	0.6 (3)
O1—C8—C9—C10	−179.52 (16)	N2—C23—C24—C20	−0.3 (2)
C13—C8—C9—C10	−0.2 (3)	C22—C23—C24—C20	−179.20 (16)
N1—C9—C10—C11	179.77 (16)	C19—C20—C24—C23	179.2 (2)
C8—C9—C10—C11	−1.1 (3)	C21—C20—C24—C23	0.18 (19)
N1—C9—C10—C6	−0.63 (19)	C19—C20—C24—C25	−0.6 (4)
C8—C9—C10—C6	178.49 (16)	C21—C20—C24—C25	−179.59 (19)
C5—C6—C10—C11	1.2 (4)	C23—C24—C25—C26	−1.3 (3)
C7—C6—C10—C11	179.77 (19)	C20—C24—C25—C26	178.46 (19)
C5—C6—C10—C9	−178.36 (19)	C24—C25—C26—C27	0.5 (3)
C7—C6—C10—C9	0.24 (19)	O3—C22—C27—C26	178.33 (17)
C9—C10—C11—C12	1.6 (3)	C23—C22—C27—C26	−1.6 (3)
C6—C10—C11—C12	−177.90 (19)	O3—C22—C27—C28	−4.1 (3)
C10—C11—C12—C13	−0.8 (3)	C23—C22—C27—C28	175.89 (16)
O1—C8—C13—C12	−179.70 (16)	C25—C26—C27—C22	1.0 (3)
C9—C8—C13—C12	1.0 (3)	C25—C26—C27—C28	−176.49 (18)
O1—C8—C13—C14	2.4 (3)	C22—C27—C28—O4	0.3 (3)
C9—C8—C13—C14	−176.92 (16)	C26—C27—C28—O4	177.80 (19)
C11—C12—C13—C8	−0.5 (3)	C8—C9—N1—C7	−178.24 (18)
C11—C12—C13—C14	177.38 (17)	C10—C9—N1—C7	0.8 (2)
C8—C13—C14—O2	−3.4 (3)	C2—C7—N1—C9	179.03 (18)
C12—C13—C14—O2	178.69 (18)	C6—C7—N1—C9	−0.6 (2)
C21—C16—C17—C18	−0.4 (3)	C22—C23—N2—C21	179.13 (17)
C15—C16—C17—C18	179.59 (18)	C24—C23—N2—C21	0.4 (2)
C16—C17—C18—C19	−0.1 (3)	C16—C21—N2—C23	−178.75 (18)
C17—C18—C19—C20	0.3 (3)	C20—C21—N2—C23	−0.3 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O3^{i}	0.93	2.50	3.254 (2)	138
N1—H1···O4^{ii}	0.87 (2)	2.00 (2)	2.862 (2)	174 (2)
O1—H1*D*···O2	0.94 (3)	1.74 (3)	2.602 (2)	151 (3)
N2—H2···O2^{iii}	0.91 (2)	1.97 (2)	2.879 (2)	173 (2)
O3—H3*A*···O4	0.90 (3)	1.78 (3)	2.595 (2)	150 (3)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) *x*, *y*+1, *z*.