Crystal structure, Hirshfeld surface and frontier molecular orbital analysis of 10-benzyl-9-(4-hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione

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In the fused ring system of the title molecule, C31H35NO4, the conformation of the central dihydropyridine ring is intermediate between boat and envelope with the N and the opposite C atoms lying out of the basal plane. The conformations of terminal rings are close to envelope, with the atoms substituted by two methyl groups as the flaps. In the crystal, the molecules are linked by O—H⋯O hydrogen bonds into helical chains. The Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H⋯C (63.2%), O⋯H⋯H⋯O (20.1%) and C⋯H⋯C (14.4%) contacts. Quantum chemical calculations of the frontier molecular orbitals were carried out to characterize the chemical reactivity of the title compound.

1. Chemical context

The acridine fragment is a part of a number of naturally occurring substances, and its derivatives have been used as photoinitiators. Acridine-1,8-diones have been shown to have very high lasing efficiencies and have been used as dyes (Niknam & Damya, 2009). Some acridine derivatives (Nasim & Brychc, 1979; Thull & Testa, 1994), also well known as therapeutic agents, have a wide range of applications in the pharmaceutical and dye industries. These include compounds that are used as anti-cancer (Sondhi et al., 2004; Sugaya et al., 1994; Kimura et al., 1993), anti-tubercular (Aly & Abadi, 2004; Tripathi et al., 2006), anti-inflammatory (Chen et al., 2002), anti-malarial (Kumar et al., 2009; Tomar et al., 2010), anti-viral (Gupta & Jaiswal, 2010; Tonelli et al., 2011), anti-parasitic (Di Giorgio, et al., 2005) and fungicidal agents (Srivastava & Nizamuddin, 2004). In this context, we report here the synthesis, crystal structure, Hirshfeld surface and frontier molecular orbital analysis of the title acridine-1,8-dione derivative.

2. Structural commentary

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The conformation of the central
The dihydropyridine ring is intermediate between boat and envelope: four atoms (C8, C9, C17 and C18) form the basal plane with a deviation of 0.008 (2) Å for all of them, whereas atoms N1 and C16 deviate from this plane by 0.168 (2) and 0.476 (2) Å, respectively. The conformations of the terminal C8–C13 and C17–C22 rings are close to envelope with C12 and C20, respectively, as the flap atoms. The basal planes of these envelopes are twisted, and the deviations of corresponding atoms from their least-squares planes are between 0.005 (2) and 0.100 (2) Å. The N1 atom has an essentially planar environment, deviating from the plane through atoms C7, C8 and C18 by only 0.018 (2) Å. The bond lengths in the N1--C8--C9--C10--O2 and N1--C18--C17--C22--O1 chains indicate π-conjugation of N1 with the carbonyl groups C10=O2 and C22=O1 (Table 1). All other bond lengths and angles in the title structure are within the ranges normal for analogous compounds (Allen et al., 1987; Thamotharan et al., 2021; Allah et al., 2021; Mohamed et al., 2013; Akkurt et al., 2014).

3. Supramolecular features and Hirshfeld analysis

In the crystal, the molecules are linked via O3—H3A···O1i hydrogen bonds [symmetry code (i): $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$] forming helical chains along the b-axis direction (Fig. 2, Table 2). The chains are further connected by weak C7—H7B···O1ii hydrogen bonds [symmetry code (ii): $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$] forming sheets parallel to (101).

To quantify the intermolecular contacts in the crystal, Hirshfeld surfaces and two-dimensional fingerprint plots were generated using Crystal Explorer (Version 17.5; Turner et al., 2017). The Hirshfeld surface mapped over $d_{norm}$ in the range −0.436 to 1.583 a.u. (Fig. 3) show the intermolecular contacts as red-coloured spots, which indicate C—H···O and O—H···O hydrogen bonds. The red and blue regions corresponding to negative (hydrogen-bond acceptors) and positive (hydrogen-bond donors) potentials on the Hirshfeld surface mapped over electrostatic potential are shown in Fig. 4. The two-dimensional fingerprint plots are presented in Fig. 5. The H···H contacts comprise 63.2% of the total interactions.

### Table 1

| Bond          | Length (Å) |
|---------------|------------|
| C8—C9        | 1.365 (3)  |
| C8—N1        | 1.404 (3)  |
| C9—C10       | 1.462 (3)  |
| C10—O2       | 1.236 (3)  |
| C17—C18      | 1.367 (3)  |
| C17—C22      | 1.459 (3)  |
| C18—N1       | 1.400 (3)  |
| C22—O1       | 1.240 (3)  |

### Table 2

| Hydrogen-bond geometry (Å, °) |
|-------------------------------|
| $D$—$H$···$A$ | $D$—$H$ | $H$···$A$ | $D$···$A$ | $D$—$H$···$A$ |
|-----------------|--------|---------|---------|----------------|
| O3—H3A···O1i    | 0.94 (4)| 2.07 (4)| 2.780 (2)| 131 (3)        |
| C7—H7B···O1ii  | 0.97   | 2.41    | 3.260 (3)| 146            |

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$
Besides these contacts, O⋯H/H⋯O (20.1%) and C⋯H/H⋯C (14.4%) interactions make significant contributions to the total Hirshfeld surface. The percentage contributions of the N⋯C/C⋯N, C⋯O/H⋯O, and C⋯C contacts are 0.3, 1.2 and 0.5%, respectively.

4. Frontier molecular orbital analysis

The chemical reactivity of the title compound was studied by frontier molecular orbital analysis. For the calculation, the molecular structure obtained from X-ray diffraction data was used as the molecular model. The energy levels, summarized in Table 3, were computed at the DFT-B3LYP/6-311G++(d,p) level of theory as implemented in Gaussian09W (Frisch et al., 2013). The calculated frontier molecular orbitals, LUMO+1, LUMO, HOMO, and HOMO−1, are shown in Fig. 6. The energies of LUMO+1, LUMO, HOMO and HOMO−1 were calculated to be −0.9021, −1.7652, −5.5800 and −5.9005 eV, respectively, and the energies required to excite one electron from HOMO−1 to LUMO+1 and from HOMO to LUMO are 4.9984 and 3.8148 eV, respectively. The chemical hardness, chemical potential, chemical softness and electrophilicity.
index of the title molecule are listed in Table 4. The electrophilicity index value of 3.3429 eV shows the global electrophilic nature of the molecule. Based on the wide band gap and chemical hardness value of 2.0174 eV, the title molecule seems to be hard.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, updated September 2021; Groom et al., 2016) for the acridine-1,8(2H)dione unit resulted in 22 hits. They include the following acridine-1,8(2H)dione derivatives similar to the title compound: 4-ethoxyphenyl (QEDYAB; Sughanya & Sureshbabu, 2012), 3,4-dimethoxyphenyl (PUSJEU; Sureshbabu & Sughanya, 2015) and 3-ethoxy-4-hydroxyphenyl (MULWUO; Suresh Babu et al., 2020). In the title compound, the dihedral angle between the phenyl and dihydropyridine rings is 85.39 (2)°/C14, similar to the values observed for the 4-ethoxyphenyl analogue QEDYAB, the 3,4-dimethoxyphenyl analogue PUSJEU, and 3-ethoxy-4-hydroxyphenyl analogue MULWUO, for which the dihedral angles are 75.20 (4), 89.47 (9) and 85.81 (2)°/C14, respectively.

6. Synthesis and crystallization

A mixture of benzylamine (0.214g, 2 mmol), 4-hydroxy-3-methoxybenzaldehyde (0.304g, 2 mmol) and 5,5-dimethylcyclohexane-1,3-dione (0.56g, 4 mmol) was dissolved in 25 ml of acetic acid. The solution was refluxed for 2 h with the reaction being monitored by TLC. After the reaction was about to the end, the reaction mixture was poured into 150 ml of ice-cold water, stirred at 298–303K for 10 min and then kept at room temperature for 12 h. The solid was filtered, washed repeatedly with water and dried. Yellow single crystals suitable for X-ray diffraction were obtained from 95% ethanol (m.p. 483 K, 0.718 g, 1.48 mmol, yield 74%). IR (KBr): cm⁻¹ 2957-2871, 1634, 1455, 1373. ¹H NMR(400 MHz, CDCl₃): 0.90 (s, 6H), 0.99 (s, 6H), 2.21 (s, 4H), 2.40 (dd, 4H), 3.86 (s, 3H), 4.90 (s, 2H), 5.24 (s, 1H), 5.51 (s, 1H), 6.56 (d, 1H), 6.70 (d, 1H), 7.12 (d, 1H), 7.17 (s, 2H), 7.35–7.40 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): 28.11, 28.65, 31.70, 32.73, 40.27, 48.73, 50.05, 55.88, 111.90, 113.60, 115.44, 119.45, 125.38, 128.01, 129.25, 137.10, 138.36, 143.69, 145.92, 150.31, 195.90. ESI–MS: m/z:485.12 [M + H]⁺.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. Hydrogen atoms were fixed geometrically and treated as riding atoms, with C—H = 0.93–0.97 Å and Uₐw(H) = 1.2Uₑq(C) or 1.5Uₑq(C-methyl).

Acknowledgements

The authors thank Dr Sudhadevi Antharjanam and SAIF, IIT Madras, for the intensity data collection.
Table 5

Experimental details.

| Crystal data        |       |
|---------------------|-------|
| Chemical formula    | C₁₅H₂₁NO₄ |
| M₀                  | 248.36  |
| Crystal system, space group | Monoclinic, P2₁/a |
| Temperature (K)     | 296    |
| a, b, c (Å)         | 10.4430 (6), 18.4563 (11), 14.2378 (9) |
| β (°)               | 107.930 (2) |
| V (Å³)              | 2610.93 (3) |
| Z                   | 4      |
| Radiation type      | Mo Kα  |
| μ (mm⁻¹)            | 0.08   |
| Crystal size (mm)   | 0.40 × 0.30 × 0.20 |

Data collection

| Diffractometer      | Bruker Kappa APEXII |
|---------------------|--------------------|
| Absorption correction | Multi-scan (SADABS, Bruker, 2016) |
| Tmin, Tmax          | 0.953, 0.982 |
| No. of observed reflections | 37271, 5135, 3061 |
| Rint               | 0.096 |
| (sinθ/λ)max (Å⁻¹)  | 0.617 |

Refinement

| R[F² > 2σ(F²)] , wR(F²) , S | 0.052, 0.145, 1.02 |
| No. of reflections          | 5135 |
| No. of parameters           | 330  |
| H-atom treatment            | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³)        | 0.19, −0.19 |

Research communications

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Crystal structure, Hirshfeld surface and frontier molecular orbital analysis of 10-benzyl-9-(4-hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione

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Computing details

Data collection: APEX2 (Bruker, 2016); cell refinement: APEX2 and SAINT (Bruker, 2016); data reduction: SAINT and XPREP (Bruker, 2016); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015b) and publCIF (Westrip, 2010).

10-Benzyl-9-(4-hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione

Crystal data

C₃₁H₃₅NO₄, M_r = 485.60
Monoclinic, P2_1/n
a = 10.4430 (6) Å
b = 18.4563 (11) Å
c = 14.2378 (9) Å
β = 107.930 (2)°
V = 2610.9 (3) Å³
Z = 4
F(000) = 1040

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan
(SADABS; Bruker, 2016)

37271 measured reflections
5135 independent reflections
3061 reflections with I > 2σ(I)
R(int) = 0.096
θ(max) = 26.0°, θ(min) = 1.9°
h = −12→12
k = −22→22
l = −17→17
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.145$
$S = 1.02$
5135 reflections
330 parameters
0 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma(F_o^2) + (0.049P)^2 + 1.0354P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.19$ e $\text{Å}^{-3}$
$\Delta\rho_{\text{min}} = -0.19$ e $\text{Å}^{-3}$

Extinction correction: SHELXL-2018
(Sheldrick 2015b),
$F_c^* = kF_c[1+0.001xF_c^2/\lambda^3\sin(2\theta)]^{1/4}$
Extinction coefficient: 0.0095 (9)

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 | 0.4603 (3) | 0.09167 (14) | 0.35227 (19) | 0.0494 (7) |
| H1 | 0.410397 | 0.089768 | 0.396205 | 0.059* |
| C2 | 0.5467 (3) | 0.03535 (15) | 0.3501 (2) | 0.0594 (8) |
| H2 | 0.554683 | -0.003955 | 0.392392 | 0.071* |
| C3 | 0.6205 (3) | 0.03758 (19) | 0.2855 (3) | 0.0730 (9) |
| H3 | 0.678749 | -0.000235 | 0.284067 | 0.088* |
| C4 | 0.6087 (3) | 0.0954 (2) | 0.2230 (3) | 0.0783 (10) |
| H4 | 0.658479 | 0.096554 | 0.178917 | 0.094* |
| C5 | 0.5225 (3) | 0.15239 (16) | 0.2254 (2) | 0.0600 (8) |
| H5 | 0.515644 | 0.191685 | 0.183241 | 0.072* |
| C6 | 0.4467 (2) | 0.15115 (13) | 0.28985 (17) | 0.0387 (6) |
| C7 | 0.3509 (2) | 0.21207 (12) | 0.29182 (16) | 0.0373 (6) |
| H7A | 0.363873 | 0.251425 | 0.250493 | 0.045* |
| C8 | 0.2902 (2) | 0.21609 (11) | 0.44966 (16) | 0.0315 (5) |
| C9 | 0.3279 (2) | 0.22925 (11) | 0.54880 (16) | 0.0324 (5) |
| C10 | 0.2338 (2) | 0.21768 (12) | 0.60510 (18) | 0.0397 (6) |
| C11 | 0.0907 (2) | 0.19725 (14) | 0.54753 (19) | 0.0486 (7) |
| H11A | 0.040547 | 0.240759 | 0.520922 | 0.058* |
| H11B | 0.048053 | 0.174697 | 0.591747 | 0.058* |
| C12 | 0.0856 (2) | 0.14502 (13) | 0.46279 (18) | 0.0415 (6) |
| C13 | 0.1588 (2) | 0.17948 (13) | 0.39549 (17) | 0.0387 (6) |
| H13A | 0.176286 | 0.142145 | 0.353090 | 0.046* |
| H13B | 0.099539 | 0.214945 | 0.353460 | 0.046* |
| C14 | 0.1542 (3) | 0.07360 (14) | 0.5055 (2) | 0.0621 (8) |
| H14A | 0.151247 | 0.040740 | 0.452607 | 0.093* |
| H14B | 0.246283 | 0.082828 | 0.542975 | 0.093* |
| H14C | 0.108158 | 0.052524 | 0.547691 | 0.093* |
### Atomic displacement parameters (Å²)

|     | U₁¹  | U₂²  | U₃³  | U₁²  | U₁₃  | U₂₃  |
|-----|------|------|------|------|------|------|
| C1  | 0.0509 (15) | 0.0494 (16) | 0.0490 (16) | 0.0025 (13) | 0.0172 (13) | −0.0031 (13) |
| N1  | 0.37180 (17) | 0.23959 (9) | 0.39359 (13) | 0.0323 (4)  |      |      |
| O1  | 0.61215 (17) | 0.39158 (9) | 0.65671 (12) | 0.0508 (5)  |      |      |
| O2  | 0.26832 (18) | 0.22551 (11) | 0.69568 (13) | 0.0585 (5)  |      |      |
| O3  | 0.82731 (18) | 0.01471 (9) | 0.72534 (15) | 0.0533 (5)  |      |      |
| O4  | 0.68627 (18) | 0.06155 (9) | 0.84518 (13) | 0.0554 (5)  |      |      |
| H3A | 0.819 (3) | −0.009 (2) | 0.782 (3) | 0.113 (14)* |      |      |

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sup-3
C2 0.0593 (18) 0.0502 (17) 0.0631 (19) 0.0088 (14) 0.0105 (15) −0.0073 (15)
C3 0.065 (2) 0.075 (2) 0.076 (2) 0.0198 (17) 0.0177 (18) −0.0218 (19)
C4 0.074 (2) 0.100 (3) 0.075 (2) 0.011 (2) 0.0425 (18) −0.017 (2)
C5 0.0650 (18) 0.072 (2) 0.0508 (17) −0.0001 (16) 0.0284 (14) −0.0038 (15)
C6 0.0358 (12) 0.0447 (14) 0.0335 (13) −0.0070 (11) 0.0076 (10) −0.0110 (11)
C7 0.0415 (13) 0.0401 (13) 0.0287 (12) −0.0049 (11) 0.0087 (10) −0.0021 (10)
C8 0.0337 (12) 0.0270 (11) 0.0333 (12) 0.0029 (9) 0.0093 (10) 0.0006 (10)
C9 0.0344 (12) 0.0309 (12) 0.0322 (12) 0.0036 (10) 0.0105 (10) 0.0020 (10)
C10 0.0458 (14) 0.0376 (13) 0.0374 (14) 0.0045 (11) 0.0155 (11) 0.0015 (11)
C11 0.0424 (14) 0.0537 (16) 0.0537 (16) −0.0016 (12) 0.0206 (12) −0.0004 (13)
C12 0.0395 (13) 0.0406 (14) 0.0444 (14) −0.0046 (11) 0.0130 (11) 0.0014 (11)
C13 0.0370 (13) 0.0393 (13) 0.0376 (13) −0.0032 (11) 0.0083 (10) 0.0000 (11)
C14 0.0470 (16) 0.0685 (19) 0.0685 (19) 0.0007 (14) 0.0221 (16) 0.0101 (14)
C15 0.0470 (16) 0.078 (2) 0.0665 (19) −0.0225 (15) 0.0166 (14) −0.0063 (16)
C16 0.0373 (12) 0.0299 (12) 0.0276 (11) 0.0019 (10) 0.0078 (9) −0.0025 (9)
C17 0.0331 (12) 0.0281 (11) 0.0320 (12) 0.0007 (9) 0.0071 (10) −0.0003 (10)
C18 0.0306 (11) 0.0278 (11) 0.0335 (12) 0.0014 (9) 0.0065 (9) 0.0018 (10)
C19 0.0423 (13) 0.0375 (13) 0.0369 (13) −0.0016 (11) 0.0118 (11) 0.0041 (11)
C20 0.0435 (14) 0.0367 (14) 0.0441 (14) −0.0068 (11) 0.0163 (11) 0.0004 (11)
C21 0.0626 (17) 0.0523 (16) −0.0116 (12) 0.0228 (13) −0.0058 (12)
C22 0.0352 (12) 0.0318 (12) 0.0390 (14) 0.0019 (10) 0.0071 (10) −0.0030 (11)
C23 0.0392 (14) 0.0672 (19) 0.0686 (19) 0.0025 (13) 0.0164 (13) 0.0030 (16)
C24 0.0667 (18) 0.0613 (19) −0.0174 (14) 0.0277 (15) 0.0053 (14)
C25 0.0310 (12) 0.0289 (12) 0.0328 (12) −0.0031 (9) 0.0035 (10) −0.0020 (10)
C26 0.0447 (14) 0.0349 (13) 0.0344 (13) 0.0041 (11) 0.0110 (11) 0.0050 (10)
C27 0.0467 (14) 0.0387 (14) 0.0445 (15) 0.0076 (11) 0.0188 (12) 0.0031 (12)
C28 0.0379 (13) 0.0298 (12) 0.0425 (14) 0.0028 (10) 0.0055 (11) 0.0017 (11)
C29 0.0429 (13) 0.0327 (12) 0.0309 (12) −0.0008 (10) 0.0078 (10) 0.0066 (10)
C30 0.0413 (13) 0.0328 (12) 0.0336 (13) −0.0001 (10) 0.0106 (10) −0.0014 (10)
C31 0.117 (3) 0.072 (2) 0.0530 (18) 0.0312 (19) 0.0444 (19) 0.0244 (16)
N1 0.0347 (10) 0.0340 (10) 0.0270 (10) −0.0035 (8) 0.0078 (8) −0.0013 (8)
O1 0.0639 (12) 0.0427 (10) 0.0406 (10) −0.0104 (8) 0.0084 (8) −0.0098 (8)
O2 0.0616 (12) 0.0802 (14) 0.0377 (10) −0.0048 (10) 0.0213 (9) −0.0042 (10)
O3 0.0598 (12) 0.0433 (10) 0.0583 (12) 0.0200 (9) 0.0205 (10) 0.0155 (9)
O4 0.0753 (13) 0.0514 (11) 0.0431 (10) 0.0193 (9) 0.0236 (9) 0.0164 (9)

Geometric parameters (Å, °)

C1—C2 1.383 (3) C16—H16 0.9800
C1—C6 1.392 (3) C17—C18 1.367 (3)
C1—H1 0.9300 C17—C22 1.459 (3)
C2—C3 1.371 (4) C18—N1 1.400 (3)
C2—H2 0.9300 C18—C19 1.513 (3)
C3—C4 1.370 (5) C19—C20 1.535 (3)
C3—H3 0.9300 C19—H19A 0.9700
C4—C5 1.392 (4) C19—H19B 0.9700
C4—H4 0.9300 C20—C21 1.528 (3)
C5—C6 1.384 (3) C20—C24 1.531 (3)
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| C5—H5        | 0.9300       | C20—C23      | 1.538 (3)    |
| C6—C7        | 1.511 (3)    | C21—C22      | 1.512 (3)    |
| C7—N1        | 1.487 (3)    | C21—H21A     | 0.9700       |
| C7—H7A       | 0.9700       | C21—H21B     | 0.9700       |
| C7—H7B       | 0.9700       | C22—O1       | 1.240 (3)    |
| C8—C9        | 1.365 (3)    | C23—H23A     | 0.9600       |
| C8—N1        | 1.404 (3)    | C23—H23B     | 0.9600       |
| C8—C13       | 1.511 (3)    | C23—H23C     | 0.9600       |
| C9—C10       | 1.462 (3)    | C24—H24A     | 0.9600       |
| C9—C16       | 1.522 (3)    | C24—H24B     | 0.9600       |
| C10—O2       | 1.236 (3)    | C24—H24C     | 0.9600       |
| C10—C11      | 1.514 (3)    | C25—C26      | 1.387 (3)    |
| C11—C12      | 1.532 (3)    | C25—C30      | 1.407 (3)    |
| C11—H11A     | 0.9700       | C26—C27      | 1.393 (3)    |
| C11—H11B     | 0.9700       | C26—H26      | 0.9300       |
| C12—C14      | 1.534 (3)    | C27—C28      | 1.380 (3)    |
| C12—C13      | 1.535 (3)    | C27—H27      | 0.9300       |
| C12—C15      | 1.537 (3)    | C28—O3       | 1.376 (3)    |
| C13—H13A     | 0.9700       | C28—C29      | 1.396 (3)    |
| C13—H13B     | 0.9700       | C29—O4       | 1.383 (3)    |
| C14—H14A     | 0.9600       | C29—C30      | 1.393 (3)    |
| C14—H14B     | 0.9600       | C30—H30      | 0.9300       |
| C14—H14C     | 0.9600       | C31—O4       | 1.415 (3)    |
| C15—H15A     | 0.9600       | C31—H31A     | 0.9600       |
| C15—H15B     | 0.9600       | C31—H31B     | 0.9600       |
| C15—H15C     | 0.9600       | C31—H31C     | 0.9600       |
| C16—C17      | 1.512 (3)    | O3—H3A       | 0.94 (4)     |
| C16—C25      | 1.541 (3)    |              |              |
| C2—C1—C6     | 121.2 (3)    | C18—C17—C22  | 119.6 (2)    |
| C2—C1—H1     | 119.4        | C18—C17—C16  | 120.02 (19)  |
| C6—C1—H1     | 119.4        | C22—C17—C16  | 120.38 (19)  |
| C3—C2—C1     | 119.9 (3)    | C17—C18—N1   | 119.9 (2)    |
| C3—C2—H2     | 120.1        | C17—C18—C19  | 122.82 (19)  |
| C1—C2—H2     | 120.1        | N1—C18—C19   | 117.30 (18)  |
| C4—C3—C2     | 120.2 (3)    | C18—C19—C20  | 114.28 (18)  |
| C4—C3—H3     | 119.9        | C18—C19—H19A | 108.7        |
| C2—C3—H3     | 119.9        | C20—C19—H19A | 108.7        |
| C3—C4—C5     | 120.1 (3)    | C18—C19—H19B | 108.7        |
| C3—C4—H4     | 119.9        | C20—C19—H19B | 108.7        |
| C5—C4—H4     | 119.9        | H19A—C19—H19B | 107.6      |
| C6—C5—C4     | 120.7 (3)    | C21—C20—C24  | 109.8 (2)    |
| C6—C5—H5     | 119.7        | C21—C20—C19  | 107.77 (19)  |
| C4—C5—H5     | 119.7        | C24—C20—C19  | 108.7 (2)    |
| C5—C6—C1     | 118.0 (2)    | C21—C20—C23  | 110.8 (2)    |
| C5—C6—C7     | 121.1 (2)    | C24—C20—C23  | 108.9 (2)    |
| C1—C6—C7     | 120.9 (2)    | C19—C20—C23  | 110.8 (2)    |
| N1—C7—C6     | 111.90 (18)  | C22—C21—C20  | 113.29 (19)  |
N1—C7—H7A 109.2 C22—C21—H21A 108.9
C6—C7—H7A 109.2 C20—C21—H21A 108.9
N1—C7—H7B 109.2 C22—C21—H21B 108.9
C6—C7—H7B 109.2 C20—C21—H21B 108.9
H7A—C7—H7B 107.9 H21A—C21—H21B 107.7
C9—C8—N1 120.03 (19) O1—C22—C17 122.0 (2)
C9—C8—C13 122.3 (2) O1—C22—C21 120.7 (2)
N1—C8—C13 117.57 (19) C17—C22—C21 117.3 (2)
C8—C9—C10 120.8 (2) C20—C23—H23A 109.5
C8—C9—C16 119.9 (2) C20—C23—H23B 109.5
C10—C9—C16 119.26 (19) H23A—C23—H23B 109.5
O2—C10—C9 121.7 (2) C20—C23—H23C 109.5
O2—C10—C11 121.1 (2) H23A—C23—H23C 109.5
C9—C10—C11 117.2 (2) H23B—C23—H23C 109.5
C10—C11—C12 111.8 (2) C26—C25—C30 118.0 (2)
C10—C11—H11A 109.2 C20—C24—H24A 109.5
C12—C11—H11A 109.2 C20—C24—H24B 109.5
C10—C11—H11B 109.2 H24A—C24—H24B 109.5
C12—C11—H11B 109.2 H24A—C24—H24C 109.5
C11—C12—C13 109.0 (2) C28—C27—C26 120.9 (2)
C11—C12—C14 110.0 (2) C28—C27—H27 119.6
C14—C12—C13 111.2 (2) C28—C27—H27 119.6
C14—C12—C15 109.2 (2) C30—C27—C26 120.8 (2)
C13—C12—C14 108.1 (2) C30—C27—H27 119.6
C8—C13—C12 114.50 (19) C30—C27—H27 119.6
C8—C13—H13A 108.6 C26—C27—H27 118.0 (2)
C12—C13—H13A 108.6 C26—C27—H27 118.0 (2)
C8—C13—H13B 108.6 O3—C28—C27 123.1 (2)
C12—C13—H13B 108.6 O3—C28—C27 123.1 (2)
H13A—C13—H13B 107.6 C27—C28—C29 119.0 (2)
C12—C14—H14A 109.5 C27—C28—C29 119.0 (2)
C12—C14—H14B 109.5 O4—C29—C30 125.5 (2)
H14A—C14—H14B 109.5 O4—C29—C30 125.5 (2)
H14A—C14—H14C 109.5 C30—C29—C28 114.2 (2)
C12—C14—H14C 109.5 C30—C29—C28 114.2 (2)
H14B—C14—H14C 109.5 C30—C29—C28 114.2 (2)
C12—C15—H15A 109.5 C25—C30—C29 120.3 (2)
C12—C15—H15B 109.5 C25—C30—C29 120.3 (2)
H15A—C15—H15B 109.5 C25—C30—C29 120.3 (2)
C12—C15—H15C 109.5 C25—C30—C29 120.3 (2)
H15A—C15—H15C 109.5 C25—C30—C29 120.3 (2)
H15B—C15—H15C 109.5 C25—C30—C29 120.3 (2)
C17—C16—C9 106.92 (17) C18—N1—C8 119.06 (18)
C17—C16—C25 113.24 (18) C18—N1—C7 119.81 (18)
C9—C16—C25 111.08 (17) C8—N1—C7 121.08 (17)
C17—C16—H16 108.5 C28—O3—H3A 112 (2)
C9—C16—H16 108.5  
C25—C16—H16 108.5  
C6—C1—C2—C3 −0.1 (4)  
C1—C2—C3—C4 −0.1 (5)  
C2—C3—C4—C5 0.5 (5)  
C3—C4—C5—C6 −0.7 (5)  
C4—C5—C6—C1 0.4 (4)  
C4—C5—C6—C7 −178.9 (2)  
C2—C1—C6—C5 −0.1 (4)  
C2—C1—C6—C7 179.3 (2)  
C5—C6—C7—N1 −129.5 (2)  
C1—C6—C7—N1 51.1 (3)  
N1—C8—C9—C10 168.45 (19)  
C13—C8—C9—C10 −8.8 (3)  
N1—C8—C9—C16 −11.7 (3)  
C13—C8—C9—C16 171.10 (19)  
C8—C9—C10—O2 −3.9 (3)  
C16—C9—C10—O2 176.0 (2)  
C6—C7—N1—C8 51.1 (3)  
N1—C8—C9—C16 171.05 (19)  
N1—C8—C9—C10 168.45 (19)  
C13—C8—C9—C10 −8.8 (3)  
N1—C8—C9—C10 168.45 (19)  
C10—C11—C12—C13 −11.7 (3)  
C10—C11—C12—C13 −11.7 (3)  
C9—C8—C13—C12 38.8 (3)  
C10—C11—C12—C13 63.9 (3)  
C10—C11—C12—C13 −175.5 (2)  
C9—C8—C13—C12 38.8 (3)  
C10—C11—C12—C13 63.9 (3)  
C10—C11—C12—C13 −175.5 (2)  
N1—C8—C13—C12 −171.05 (19)  
C11—C12—C13—C8 43.4 (3)  
C14—C12—C13—C8 −76.5 (3)  
C15—C12—C13—C8 164.4 (2)  
C8—C9—C16—C17 36.7 (3)  
C10—C9—C16—C17 −143.48 (19)  
C8—C9—C16—C17 −143.48 (19)  
C10—C9—C16—C17 172.0 (2)  
C9—C16—C17—C18 −38.3 (3)  
C25—C16—C17—C18 84.3 (2)  
C9—C16—C17—C22 140.35 (19)  
C25—C16—C17—C22 −97.0 (2)  
C22—C17—C18—N1 −163.77 (18)  
C16—C17—C18—N1 14.9 (3)  
C22—C17—C18—N1 14.9 (3)  
C16—C17—C18—N1 −163.77 (18)  
C17—C18—N1—C20 10.0 (3)  
N1—C18—C19—C20 −171.28 (19)

C9—C16—H16 108.5  
C25—C16—H16 108.5  
C18—C19—C20—C21 −44.2 (3)  
C18—C19—C20—C23 77.2 (3)  
C24—C20—C21—C22 174.9 (2)  
C19—C20—C21—C22 56.6 (3)  
C23—C20—C21—C22 −64.8 (3)  
C18—C17—C22—O1 175.6 (2)  
C16—C17—C22—O1 −3.1 (3)  
C9—C16—C25—C26 −94.3 (2)  
C9—C16—C25—C30 155.81 (19)  
C9—C16—C25—C26 94.3 (2)  
C9—C16—C25—C30 −83.9 (2)  
C25—C26—C27—O3 −179.3 (2)  
C25—C26—C27—C28 0.9 (3)  
C26—C27—C28—O3 −179.3 (2)  
O3—C28—C29—O4 0.5 (3)  
C28—C29—O4—C31 −178.5 (2)  
C26—C28—C29—O4 −179.2 (2)  
C27—C28—C29—O4 1.8 (3)  
O4—C29—C30—C25 178.1 (2)  
C28—C29—C30—C25 −2.2 (3)  
C26—C29—C30—C25 1.0 (3)  
C16—C25—C30—C29 179.24 (19)  
C17—C18—N1—C8 15.0 (3)  
C19—C18—N1—C8 −163.75 (19)  
C17—C18—N1—C7 13.8 (3)  
C19—C18—N1—C7 −167.41 (19)  
C9—C8—N1—C18 −16.6 (3)  
C9—C8—N1—C18 160.74 (18)  
C9—C8—N1—C7 165.86 (19)  
C17—C18—N1—C7 −16.8 (3)  
C9—C8—N1—C18 160.74 (18)  
C9—C8—N1—C7 165.86 (19)  
C30—C29—O4—C31 −2.1 (4)  
C28—C29—O4—C31 178.3 (2)  
C16—C17—C18—N1 −163.77 (18)  
C16—C17—C18—N1 14.9 (3)  
C22—C17—C18—C19 −166.38 (19)  
C17—C18—C19—C20 10.0 (3)  
N1—C18—C19—C20 −171.28 (19)
### Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A  | D···A  | D—H···A |
|-------------|------|--------|--------|---------|
| O3—H3A···O1<sup>i</sup> | 0.94 (4) | 2.07 (4) | 2.780 (2) | 131 (3) |
| C7—H7B···O1<sup>ii</sup> | 0.97  | 2.41   | 3.260 (3) | 146     |

Symmetry codes: (i) −x+3/2, y−1/2, −z+3/2; (ii) x+1/2, −y+1/2, z−1/2.