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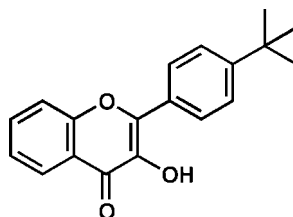
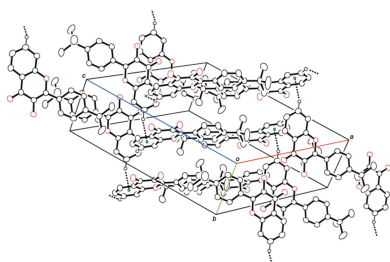
Crystal structure of 2-(4-*tert*-butylphenyl)- 3-hydroxy-4*H*-chromen-4-one

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Yellow–green fluorescent crystals of the title compound, C₁₉H₁₈O₃, were obtained by the reaction of hydroxyacetophenone and 4-*tert*-butylbenzaldehyde with hydrogen peroxide as oxidant. The plane of the benzene ring is slightly twisted to the mean plane of the 4*H*-chromene-4-one moiety (r.m.s. deviation = 0.0191 Å) by 10.53 (8)°. In the crystal, molecules are linked by pairs of O–H···O hydrogen bonds, forming inversion dimers with an R₂²(10) ring motif. The dimers are linked *via* C–H···π interactions, forming sheets parallel to (10 $\bar{1}$).

1. Chemical context

The flavonol 3-hydroxy-2-phenyl-4*H*-chromen-4-one (common name: 3-hydroxyflavone) and its derivatives are present in a wide variety of plants as phytochemical compounds (Havsteen, 1983; Aherne & O'Brien, 2002). They have been investigated for many years owing to their chemical, structural, biological and fluorescent properties (Smith *et al.*, 1968; Sengupta & Kasha, 1979; Etter *et al.*, 1986; Klymchenko & Demchenko, 2002; Pivovarenko *et al.*, 2005; Choulier *et al.*, 2010). The phenomenon of dual fluorescence due to excited states intramolecular proton transfer (ESIPT) has attracted much attention (Dick, 1987), as compounds exhibiting such properties can be used as fluorescent probes for sensing and imaging. The fluorescence of flavonols has been shown to be related to the angle between the 4*H*-chromene-4-one moiety and the attached benzene ring (Klymchenko *et al.* 2003). The effect of the intramolecular hydrogen bond of flavonols, with an OH group in position 3, for the stabilization of the molecular conformation is also important and this has been confirmed by theoretical calculations reported in a computational study on flavonoids (Aparicio, 2010). As a part of our search for new luminescent materials, we report herein on the synthesis and crystal structure of the title compound, the 4-*tert*-butylphenyl derivative of 3-hydroxyflavone.



2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The bond lengths are similar to those reported for other flavonols (Yoo *et al.*, 2014; Serdiuk *et al.*, 2013; Hino *et al.*,

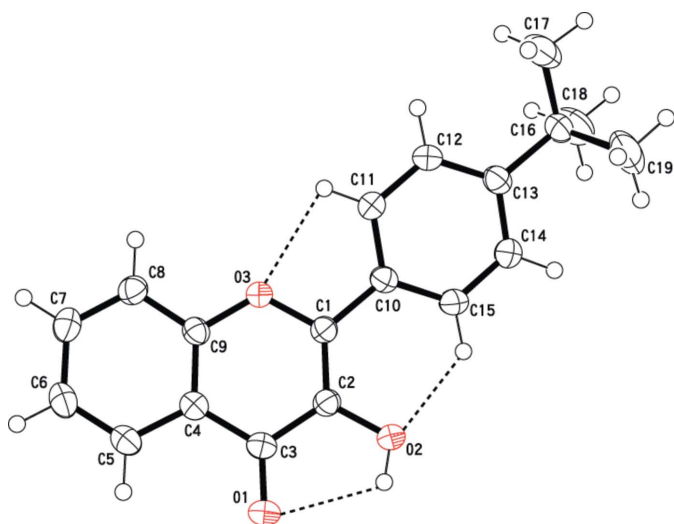


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds and short contacts are shown as dashed lines.

2013, 2011; Wera, Pivovarenko *et al.*, 2011; Wera, Serdiuk *et al.*, 2011, Wera *et al.*, 2010). The mean plane of the 4*H*-chromene-4-one moiety (O3/C1–C9; r.m.s. deviation = 0.0191 Å) is twisted by 10.53 (8)° with respect to the benzene ring (C10–C16). This relative planarity typical of the structural features of flavonols is reinforced by two intramolecular (C11–H11···O3 and C15–H15···O2) short contacts (Table 1 and Fig. 1). These intramolecular contacts lead to the molecular planarity and increase the torsional barrier, improving the π -delocalization from the 4*H*-chromene-4-one moiety toward the benzene ring. The molecule also contains an intramolecular O–H···O hydrogen bond (Table 1 and Fig. 1) with an *S*(5) ring motif.

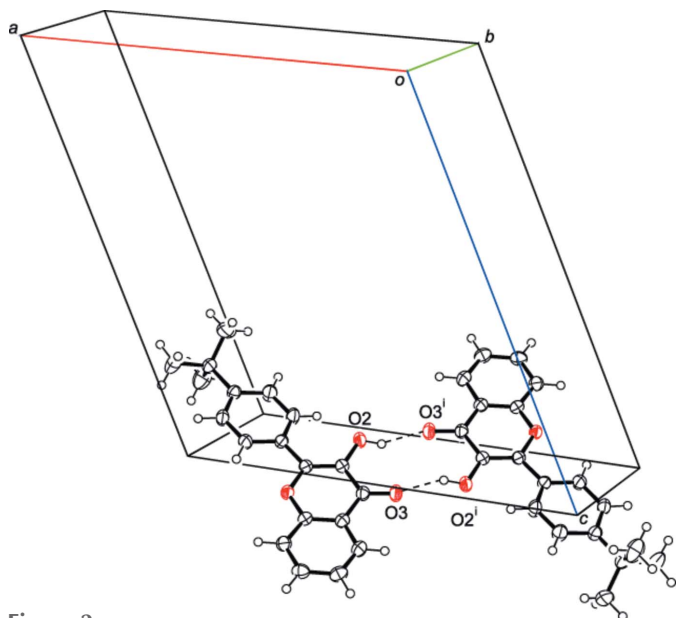


Figure 2
A view of the inversion dimer with an $R_2^2(10)$ ring motif. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

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

C_g is the centroid of the C4–C9 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|-------|-------------|-------------|---------------|
| O2–H2···O1 | 0.84 | 2.28 | 2.7262 (14) | 113 |
| C11–H11···O3 | 0.95 | 2.32 | 2.6724 (17) | 101 |
| C15–H15···O2 | 0.95 | 2.22 | 2.8508 (18) | 123 |
| O2–H2···O1 ⁱ | 0.84 | 1.96 | 2.7104 (14) | 148 |
| C7–H7··· C_g^{ii} | 0.95 | 2.59 | 3.407 (10) | 144 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{5}{2}$.

3. Supramolecular features

In the crystal of the title compound, molecules are linked *via* pairs of O–H···O hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif (Table 1 and Fig. 2). The dimers are linked by C–H··· π interactions between neighbouring molecules, forming sheets parallel to (10 $\bar{1}$); see Table 1 and Fig. 3.

4. Database survey

A search of the Cambridge Structural Database (Version 5.36, February 2015; Groom & Allen, 2014) for 3-hydroxyflavone gave 15 hits. These include 3-hydroxyflavone itself (DUMFAS; Etter *et al.*, 1986) and a number of *para*-substituted phenyl derivatives, such as the 4-aminophenyl derivative (LUBBIV; Sun, 2015), two polymorphs of the 4-(dimethylamino)phenyl derivative (BANJEH; BANJEH01: Hino *et al.*, 2011) and two polymorphs of the 4-(diethylamino)phenyl derivative (CEZDOC; CEZDOC01: Hino *et al.*, 2013). Two polymorphs of the 4-hydroxyphenyl derivative have also been reported (IJUCAS; Wera, Pivovarenko *et al.*, 2011; IKAHIM; Wera, Serdiuk *et al.*, 2011). Apart from 3-hydroxyflavone itself (DUMFAS) and the 4-aminophenyl derivative (LUBBIV), in which the phenyl ring is inclined to the mean plane of the chromen-4-one moiety by 5.5 and 4.5°, respectively, this dihedral angle in the other compounds varies from 12.3 to

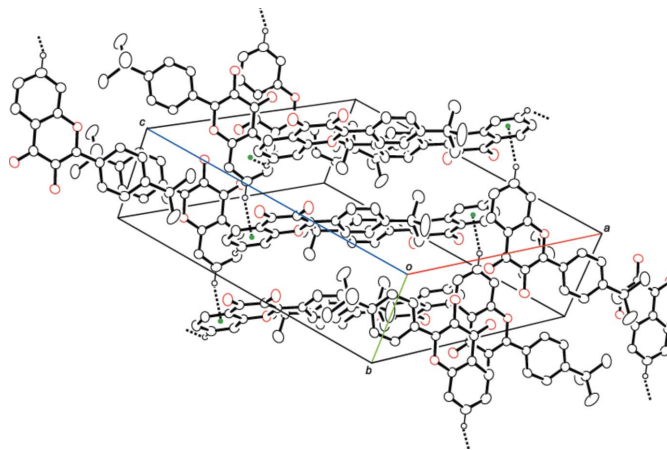


Figure 3
View of the crystal packing of the title compound. Dashed lines indicate the C–H··· π interactions (ring centroids are shown as coloured spheres; see Table 1 for details). H atoms that do not participate in these interactions have been omitted for clarity.

Table 2
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | C ₁₉ H ₁₈ O ₃ |
| <i>M</i> _r | 294.33 |
| Crystal system, space group | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> |
| Temperature (K) | 200 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 15.9735 (19), 6.1467 (7), 16.963 (2) |
| β (°) | 113.730 (1) |
| <i>V</i> (Å ³) | 1524.7 (3) |
| <i>Z</i> | 4 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 0.09 |
| Crystal size (mm) | 0.20 × 0.19 × 0.06 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD area detector |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker 2014) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.849, 0.928 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 15995, 3231, 2820 |
| <i>R</i> _{int} | 0.026 |
| (sin θ/λ) _{max} (Å ⁻¹) | 0.633 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.043, 0.127, 1.04 |
| No. of reflections | 3231 |
| No. of parameters | 203 |
| H-atom treatment | H-atom parameters constrained |
| Δρ _{max} , Δρ _{min} (e Å ⁻³) | 0.29, -0.23 |

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker 2014), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

31.2°. Hence, in DUMFAS and LUBBIV there are also short intramolecular C—H···O interactions, similar to those in the title compound. In the crystals of these two compounds, molecules are also linked *via* O—H···O hydrogen bonds, but form chains, along [001] for DUMFAS and along [100] for LUBBIV, rather than inversion dimers as in the crystal of the title compound.

5. Synthesis and crystallization

The title compound was prepared by a modification of the procedure described by Qin *et al.* (2008). 2-Hydroxyacetophenone (1 mmol) was added to a suspension of the 4-*tert*-butylbenzaldehyde (1 mmol) in ethanol (2 ml) and aqueous NaOH (6 *M*, 1 ml). The mixture was stirred at room temperature overnight. Then dilute acetic acid (30%) was added to the reaction mixture with stirring until the mixture was acidic and was cooled with an ice bath. The mixture was stirred for an additional 30 min at 273 K, and the solid precipitate obtained was collected by filtration. Hydrogen peroxide (30%, 2.6 mmol) was then added to an ice-cold suspension of the precipitate in ethanol (5 ml) and aqueous NaOH (2 *M*, 1 ml). The mixture was allowed to warm to room temperature and stirred for 4 h. The mixture was then acidified with dilute HCl (5%, 7 ml), and the precipitate formed was collected by filtration. Recrystallization from methanol

gave yellow–green fluorescing crystals. Plate-like crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in dichloromethane. ¹H NMR (400MHz, DMSO-*d*₆): δ 1.33 [*s*, 9H, C(CH₃)₃], 7.46 (*t*, 1H), 7.50 (*d*, 2H), 7.79 (*dd*, 2H), 8.13 (*dt*, 3H), 9.50 (*s*, 1H). ¹³C NMR (100MHz, DMSO-*d*₆) δ 31.4, 35.1, 118.8, 121.8, 125.1, 125.8, 128.0, 129.0, 134.1, 139.3, 146.0, 153.2, 155.0, 173.3. Fluorescent emission maxima (CH₃Cl, λ_{ex} = 365 nm): λ_{em} = 525 nm.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxyl and C-bound H atoms were included in calculated positions and treated as riding atoms: O—H = 0.84 Å, C—H = 0.95–0.98 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C,O) for the methyl and hydroxyl H atoms and 1.2*U*_{eq}(C) for other H atoms.

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supporting information

Acta Cryst. (2015). E71, 824-826 [doi:10.1107/S2056989015011482]

Crystal structure of 2-(4-*tert*-butylphenyl)-3-hydroxy-4*H*-chromen-4-one

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Computing details

Data collection: *APEX2* (Bruker 2014); cell refinement: *SAINTE* (Bruker 2014); data reduction: *SAINTE* and *XPREP* (Bruker 2014); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

2-(4-*tert*-Butylphenyl)-3-hydroxy-4*H*-chromen-4-one

Crystal data

| | |
|--------------------------------|---|
| $C_{19}H_{18}O_3$ | $F(000) = 624$ |
| $M_r = 294.33$ | $D_x = 1.282 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 15.9735 (19) \text{ \AA}$ | Cell parameters from 7083 reflections |
| $b = 6.1467 (7) \text{ \AA}$ | $\theta = 2.6\text{--}28.2^\circ$ |
| $c = 16.963 (2) \text{ \AA}$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $\beta = 113.730 (1)^\circ$ | $T = 200 \text{ K}$ |
| $V = 1524.7 (3) \text{ \AA}^3$ | Plate, yellow |
| $Z = 4$ | $0.20 \times 0.19 \times 0.06 \text{ mm}$ |

Data collection

| | |
|--|---|
| Bruker APEXII CCD area-detector diffractometer | $T_{\min} = 0.849, T_{\max} = 0.928$ |
| Radiation source: Bruker TXS fine-focus rotating anode | 15995 measured reflections |
| Bruker Helios multilayer confocal mirror monochromator | 3231 independent reflections |
| Detector resolution: 8.333 pixels mm^{-1} | 2820 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.026$ |
| Absorption correction: multi-scan (<i>SADABS</i> ; Bruker 2014) | $\theta_{\max} = 26.7^\circ, \theta_{\min} = 1.5^\circ$ |
| | $h = -20 \rightarrow 20$ |
| | $k = -7 \rightarrow 7$ |
| | $l = -21 \rightarrow 21$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | H-atom parameters constrained |
| $wR(F^2) = 0.127$ | $w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.6235P]$ |
| $S = 1.04$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 3231 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 203 parameters | $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | |

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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

4.7085 (0.0060) x + 3.2010 (0.0016) y + 10.4295 (0.0043) z = 14.3715 (0.0031)

* 0.0005 (0.0010) C1 * -0.0361 (0.0011) C2 * -0.0027 (0.0010) C3 * 0.0247 (0.0012) C4 * 0.0176 (0.0011) C5 * -0.0080 (0.0012) C6 * -0.0234 (0.0011) C7 * -0.0098 (0.0011) C8 * 0.0146 (0.0012) C9 * 0.0226 (0.0009) O3

Rms deviation of fitted atoms = 0.0191

6.5320 (0.0088) x + 2.3353 (0.0039) y + 10.0931 (0.0080) z = 15.2731 (0.0036)

Angle to previous plane (with approximate esd) = 10.53 (0.08)

* -0.0146 (0.0010) C10 * 0.0082 (0.0011) C11 * 0.0057 (0.0011) C12 * -0.0134 (0.0011) C13 * 0.0071 (0.0011) C14 * 0.0068 (0.0011) C15

Rms deviation of fitted atoms = 0.0099

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|-------------|--------------|----------------------------------|
| C1 | 0.71865 (9) | 0.1616 (2) | 1.00398 (8) | 0.0265 (3) |
| C2 | 0.64236 (9) | 0.2637 (2) | 1.00356 (8) | 0.0276 (3) |
| C3 | 0.59399 (9) | 0.1820 (2) | 1.05367 (8) | 0.0281 (3) |
| C4 | 0.62989 (9) | -0.0175 (2) | 1.10134 (8) | 0.0278 (3) |
| C5 | 0.58831 (10) | -0.1190 (3) | 1.15059 (9) | 0.0346 (3) |
| H5 | 0.5365 | -0.0539 | 1.1552 | 0.041* |
| C6 | 0.62214 (11) | -0.3121 (3) | 1.19211 (10) | 0.0381 (3) |
| H6 | 0.5937 | -0.3802 | 1.2252 | 0.046* |
| C7 | 0.69847 (10) | -0.4080 (2) | 1.18560 (9) | 0.0351 (3) |
| H7 | 0.7214 | -0.5416 | 1.2143 | 0.042* |
| C8 | 0.74088 (10) | -0.3116 (2) | 1.13819 (9) | 0.0324 (3) |
| H8 | 0.7929 | -0.3770 | 1.1341 | 0.039* |
| C9 | 0.70584 (9) | -0.1159 (2) | 1.09627 (8) | 0.0271 (3) |
| C10 | 0.77563 (9) | 0.2243 (2) | 0.95792 (8) | 0.0274 (3) |
| C11 | 0.83993 (10) | 0.0782 (2) | 0.95235 (9) | 0.0340 (3) |
| H11 | 0.8481 | -0.0587 | 0.9805 | 0.041* |
| C12 | 0.89195 (10) | 0.1298 (3) | 0.90651 (10) | 0.0362 (3) |
| H12 | 0.9349 | 0.0266 | 0.9037 | 0.043* |
| C13 | 0.88329 (9) | 0.3279 (2) | 0.86439 (9) | 0.0307 (3) |
| C14 | 0.82088 (11) | 0.4750 (3) | 0.87277 (11) | 0.0398 (4) |
| H14 | 0.8143 | 0.6138 | 0.8463 | 0.048* |
| C15 | 0.76821 (10) | 0.4262 (2) | 0.91811 (10) | 0.0372 (3) |
| H15 | 0.7265 | 0.5313 | 0.9222 | 0.045* |
| C16 | 0.94007 (10) | 0.3875 (3) | 0.81313 (9) | 0.0347 (3) |
| C17 | 0.98436 (16) | 0.1886 (3) | 0.79140 (15) | 0.0626 (6) |
| H17A | 1.0163 | 0.2333 | 0.7554 | 0.094* |
| H17B | 0.9370 | 0.0819 | 0.7602 | 0.094* |
| H17C | 1.0282 | 0.1231 | 0.8447 | 0.094* |
| C18 | 1.01612 (14) | 0.5414 (3) | 0.86712 (15) | 0.0606 (5) |
| H18A | 0.9894 | 0.6719 | 0.8808 | 0.091* |

| | | | | |
|------|--------------|---------------|--------------|------------|
| H18B | 1.0524 | 0.5828 | 0.8347 | 0.091* |
| H18C | 1.0555 | 0.4686 | 0.9206 | 0.091* |
| C19 | 0.87973 (14) | 0.4987 (5) | 0.72920 (14) | 0.0809 (8) |
| H19A | 0.8553 | 0.6342 | 0.7420 | 0.121* |
| H19B | 0.8290 | 0.4021 | 0.6958 | 0.121* |
| H19C | 0.9160 | 0.5316 | 0.6958 | 0.121* |
| O1 | 0.52607 (7) | 0.27779 (17) | 1.05437 (7) | 0.0367 (3) |
| O2 | 0.60997 (7) | 0.44503 (17) | 0.95608 (7) | 0.0359 (3) |
| H2 | 0.5649 | 0.4923 | 0.9644 | 0.054* |
| O3 | 0.74981 (6) | -0.02683 (15) | 1.04986 (6) | 0.0306 (2) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| C1 | 0.0279 (6) | 0.0263 (6) | 0.0258 (6) | 0.0013 (5) | 0.0114 (5) | 0.0006 (5) |
| C2 | 0.0276 (6) | 0.0279 (7) | 0.0272 (6) | 0.0021 (5) | 0.0108 (5) | 0.0009 (5) |
| C3 | 0.0250 (6) | 0.0311 (7) | 0.0282 (6) | -0.0002 (5) | 0.0107 (5) | -0.0031 (5) |
| C4 | 0.0279 (6) | 0.0288 (7) | 0.0268 (6) | -0.0025 (5) | 0.0112 (5) | -0.0027 (5) |
| C5 | 0.0328 (7) | 0.0386 (8) | 0.0373 (7) | -0.0024 (6) | 0.0193 (6) | -0.0004 (6) |
| C6 | 0.0441 (8) | 0.0371 (8) | 0.0385 (8) | -0.0071 (6) | 0.0222 (7) | 0.0025 (6) |
| C7 | 0.0447 (8) | 0.0273 (7) | 0.0319 (7) | -0.0016 (6) | 0.0141 (6) | 0.0016 (6) |
| C8 | 0.0372 (7) | 0.0287 (7) | 0.0326 (7) | 0.0032 (6) | 0.0154 (6) | 0.0001 (5) |
| C9 | 0.0297 (6) | 0.0283 (7) | 0.0251 (6) | -0.0017 (5) | 0.0128 (5) | -0.0017 (5) |
| C10 | 0.0270 (6) | 0.0298 (7) | 0.0265 (6) | 0.0004 (5) | 0.0120 (5) | -0.0009 (5) |
| C11 | 0.0368 (7) | 0.0314 (7) | 0.0384 (7) | 0.0077 (6) | 0.0199 (6) | 0.0082 (6) |
| C12 | 0.0359 (7) | 0.0367 (8) | 0.0432 (8) | 0.0100 (6) | 0.0235 (7) | 0.0067 (6) |
| C13 | 0.0281 (6) | 0.0354 (7) | 0.0307 (7) | -0.0009 (5) | 0.0140 (5) | 0.0006 (5) |
| C14 | 0.0456 (9) | 0.0312 (8) | 0.0525 (9) | 0.0067 (6) | 0.0300 (8) | 0.0113 (7) |
| C15 | 0.0411 (8) | 0.0300 (7) | 0.0508 (9) | 0.0080 (6) | 0.0291 (7) | 0.0060 (6) |
| C16 | 0.0321 (7) | 0.0395 (8) | 0.0376 (7) | 0.0019 (6) | 0.0195 (6) | 0.0062 (6) |
| C17 | 0.0852 (14) | 0.0522 (11) | 0.0822 (14) | 0.0007 (10) | 0.0668 (13) | -0.0014 (10) |
| C18 | 0.0534 (11) | 0.0642 (12) | 0.0782 (13) | -0.0170 (9) | 0.0411 (10) | -0.0115 (10) |
| C19 | 0.0521 (11) | 0.144 (2) | 0.0597 (12) | 0.0286 (13) | 0.0358 (10) | 0.0514 (14) |
| O1 | 0.0309 (5) | 0.0397 (6) | 0.0455 (6) | 0.0085 (4) | 0.0214 (5) | 0.0056 (5) |
| O2 | 0.0327 (5) | 0.0376 (6) | 0.0433 (6) | 0.0125 (4) | 0.0215 (5) | 0.0132 (5) |
| O3 | 0.0333 (5) | 0.0289 (5) | 0.0352 (5) | 0.0068 (4) | 0.0198 (4) | 0.0062 (4) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|---------|-------------|
| C1—C2 | 1.3682 (18) | C11—H11 | 0.9500 |
| C1—O3 | 1.3723 (16) | C12—C13 | 1.390 (2) |
| C1—C10 | 1.4695 (18) | C12—H12 | 0.9500 |
| C2—O2 | 1.3502 (16) | C13—C14 | 1.395 (2) |
| C2—C3 | 1.4493 (18) | C13—C16 | 1.5323 (18) |
| C3—O1 | 1.2386 (16) | C14—C15 | 1.382 (2) |
| C3—C4 | 1.4537 (19) | C14—H14 | 0.9500 |
| C4—C9 | 1.3888 (19) | C15—H15 | 0.9500 |
| C4—C5 | 1.4056 (19) | C16—C18 | 1.521 (2) |

| | | | |
|-------------|-------------|---------------|-------------|
| C5—C6 | 1.375 (2) | C16—C19 | 1.523 (2) |
| C5—H5 | 0.9500 | C16—C17 | 1.530 (2) |
| C6—C7 | 1.398 (2) | C17—H17A | 0.9800 |
| C6—H6 | 0.9500 | C17—H17B | 0.9800 |
| C7—C8 | 1.376 (2) | C17—H17C | 0.9800 |
| C7—H7 | 0.9500 | C18—H18A | 0.9800 |
| C8—C9 | 1.3952 (19) | C18—H18B | 0.9800 |
| C8—H8 | 0.9500 | C18—H18C | 0.9800 |
| C9—O3 | 1.3629 (16) | C19—H19A | 0.9800 |
| C10—C15 | 1.395 (2) | C19—H19B | 0.9800 |
| C10—C11 | 1.3956 (19) | C19—H19C | 0.9800 |
| C11—C12 | 1.3840 (19) | O2—H2 | 0.8400 |
| C2—C1—O3 | 120.60 (12) | C12—C13—C14 | 116.28 (13) |
| C2—C1—C10 | 128.16 (12) | C12—C13—C16 | 122.81 (13) |
| O3—C1—C10 | 111.22 (11) | C14—C13—C16 | 120.89 (13) |
| O2—C2—C1 | 120.56 (12) | C15—C14—C13 | 122.42 (14) |
| O2—C2—C3 | 117.97 (11) | C15—C14—H14 | 118.8 |
| C1—C2—C3 | 121.47 (12) | C13—C14—H14 | 118.8 |
| O1—C3—C2 | 121.12 (13) | C14—C15—C10 | 120.67 (13) |
| O1—C3—C4 | 123.13 (12) | C14—C15—H15 | 119.7 |
| C2—C3—C4 | 115.74 (11) | C10—C15—H15 | 119.7 |
| C9—C4—C5 | 118.49 (13) | C18—C16—C19 | 109.58 (17) |
| C9—C4—C3 | 119.46 (12) | C18—C16—C17 | 107.91 (15) |
| C5—C4—C3 | 122.02 (12) | C19—C16—C17 | 108.29 (17) |
| C6—C5—C4 | 120.36 (13) | C18—C16—C13 | 108.58 (13) |
| C6—C5—H5 | 119.8 | C19—C16—C13 | 109.96 (12) |
| C4—C5—H5 | 119.8 | C17—C16—C13 | 112.48 (13) |
| C5—C6—C7 | 119.94 (13) | C16—C17—H17A | 109.5 |
| C5—C6—H6 | 120.0 | C16—C17—H17B | 109.5 |
| C7—C6—H6 | 120.0 | H17A—C17—H17B | 109.5 |
| C8—C7—C6 | 120.97 (14) | C16—C17—H17C | 109.5 |
| C8—C7—H7 | 119.5 | H17A—C17—H17C | 109.5 |
| C6—C7—H7 | 119.5 | H17B—C17—H17C | 109.5 |
| C7—C8—C9 | 118.55 (13) | C16—C18—H18A | 109.5 |
| C7—C8—H8 | 120.7 | C16—C18—H18B | 109.5 |
| C9—C8—H8 | 120.7 | H18A—C18—H18B | 109.5 |
| O3—C9—C4 | 121.80 (12) | C16—C18—H18C | 109.5 |
| O3—C9—C8 | 116.51 (12) | H18A—C18—H18C | 109.5 |
| C4—C9—C8 | 121.69 (12) | H18B—C18—H18C | 109.5 |
| C15—C10—C11 | 117.45 (12) | C16—C19—H19A | 109.5 |
| C15—C10—C1 | 122.70 (12) | C16—C19—H19B | 109.5 |
| C11—C10—C1 | 119.84 (12) | H19A—C19—H19B | 109.5 |
| C12—C11—C10 | 121.02 (13) | C16—C19—H19C | 109.5 |
| C12—C11—H11 | 119.5 | H19A—C19—H19C | 109.5 |
| C10—C11—H11 | 119.5 | H19B—C19—H19C | 109.5 |
| C11—C12—C13 | 122.10 (13) | C2—O2—H2 | 109.5 |
| C11—C12—H12 | 119.0 | C9—O3—C1 | 120.86 (10) |

| | | | |
|---------------|--------------|-----------------|--------------|
| C13—C12—H12 | 119.0 | | |
| O3—C1—C2—O2 | -177.75 (11) | O3—C1—C10—C15 | -169.26 (13) |
| C10—C1—C2—O2 | 0.6 (2) | C2—C1—C10—C11 | -167.35 (14) |
| O3—C1—C2—C3 | 2.3 (2) | O3—C1—C10—C11 | 11.16 (18) |
| C10—C1—C2—C3 | -179.29 (12) | C15—C10—C11—C12 | -2.2 (2) |
| O2—C2—C3—O1 | -1.4 (2) | C1—C10—C11—C12 | 177.44 (13) |
| C1—C2—C3—O1 | 178.52 (13) | C10—C11—C12—C13 | 0.3 (2) |
| O2—C2—C3—C4 | 178.03 (11) | C11—C12—C13—C14 | 1.7 (2) |
| C1—C2—C3—C4 | -2.04 (19) | C11—C12—C13—C16 | -179.81 (14) |
| O1—C3—C4—C9 | 179.28 (13) | C12—C13—C14—C15 | -1.8 (2) |
| C2—C3—C4—C9 | -0.15 (18) | C16—C13—C14—C15 | 179.63 (14) |
| O1—C3—C4—C5 | 1.4 (2) | C13—C14—C15—C10 | 0.0 (3) |
| C2—C3—C4—C5 | -178.04 (12) | C11—C10—C15—C14 | 2.0 (2) |
| C9—C4—C5—C6 | -0.4 (2) | C1—C10—C15—C14 | -177.57 (14) |
| C3—C4—C5—C6 | 177.48 (13) | C12—C13—C16—C18 | -102.50 (18) |
| C4—C5—C6—C7 | 0.2 (2) | C14—C13—C16—C18 | 75.92 (19) |
| C5—C6—C7—C8 | 0.2 (2) | C12—C13—C16—C19 | 137.61 (19) |
| C6—C7—C8—C9 | -0.2 (2) | C14—C13—C16—C19 | -44.0 (2) |
| C5—C4—C9—O3 | -179.91 (12) | C12—C13—C16—C17 | 16.8 (2) |
| C3—C4—C9—O3 | 2.13 (19) | C14—C13—C16—C17 | -164.73 (16) |
| C5—C4—C9—C8 | 0.4 (2) | C4—C9—O3—C1 | -1.97 (19) |
| C3—C4—C9—C8 | -177.60 (12) | C8—C9—O3—C1 | 177.77 (11) |
| C7—C8—C9—O3 | -179.77 (12) | C2—C1—O3—C9 | -0.30 (19) |
| C7—C8—C9—C4 | 0.0 (2) | C10—C1—O3—C9 | -178.94 (11) |
| C2—C1—C10—C15 | 12.2 (2) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

Cg is the centroid of the C4—C9 ring.

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|---------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O2—H2 \cdots O1 | 0.84 | 2.28 | 2.7262 (14) | 113 |
| C11—H11 \cdots O3 | 0.95 | 2.32 | 2.6724 (17) | 101 |
| C15—H15 \cdots O2 | 0.95 | 2.22 | 2.8508 (18) | 123 |
| O2—H2 \cdots O1 ⁱ | 0.84 | 1.96 | 2.7104 (14) | 148 |
| C7—H7 \cdots Cg ⁱⁱ | 0.95 | 2.59 | 3.407 (10) | 144 |

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+3/2, y-1/2, -z+5/2$.