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# 3-Hydroxy-2-(4- methylphenyl)-4H-chromen-4-one

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# 3-Hydroxy-2-(4-methylphenyl)-4*H*-chromen-4-one

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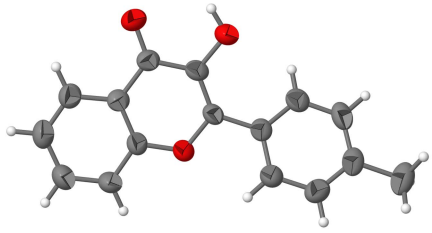
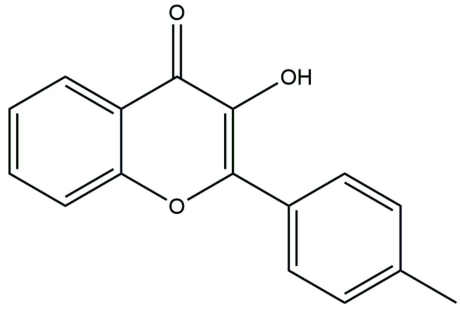
**Structural data**: full structural data are available from iucrdata.iucr.org

Our work in the area of carbon-monoxide-releasing molecules led to the synthesis and crystallization of new flavone derivatives as intermediates. Herein we report the first crystal structure of the title compound, $C_{16}H_{12}O_3$, a hydroxy-substituted flavone where the 2-phenyl group has been replaced by a *p*-tolyl group. The introduction of the 3-hydroxy group allows the formation of intermolecular O—H···O=C hydrogen bonds, used to build centrosymmetric $R_2^2(10)$ ring motifs in the crystal.

**3D view**



**Chemical scheme**




## Structure description

Flavones contain the 2-phenylbenzopyran pharmacophore and are secondary metabolites of plants. They possess many biological activities, including antibiotic, anticancer, and antioxidant behavior. Recently, there has been interest in flavones as carbon-monoxide-releasing molecules (CORMs; Anderson *et al.*, 2015). Our work in this area led to the synthesis and crystallization of flavones as intermediates. Herein we report the first crystal structure of a new 3-hydroxyflavone (Fig. 1), which forms a hydrogen-bonded dimer. The hydrogen bonding occurs between O atoms of the benzopyranone ring with an $R(10)$ synthon. The hydrogen bond between O2 and O3$^{i}$ is characterized by an O···O separation of 2.721 (2) Å [symmetry code: (i) $-x+2, -y+2, -z+1$; Table 1], and the ring motifs $R_2^2(10)$ are placed on inversion centers in the space group $P2_1/n$ (Fig. 2). A secondary intramolecular C—H···O hydrogen bond (Table 1, entry 2) also involves the hydroxy O2 atom as an acceptor group, forming an $S(6)$ motif. The centroid *Cg*1 of the tolyl ring (C10–C15) and the centroid *Cg*2 of a symmetry-related pyranone ring (C1–C4/C9/O1; symmetry code: $x, y-1, z$) are separated by 3.7525 (15) Å, with both rings almost parallel. This is the only significant $\pi$–$\pi$ interaction observed in the crystal. The molecule is nearly planar, with the tolyl and benzopyranone rings forming a dihedral angle of 18.27 (8)°. This is consistent with several other similar flavonoids, for example, 2-(4-

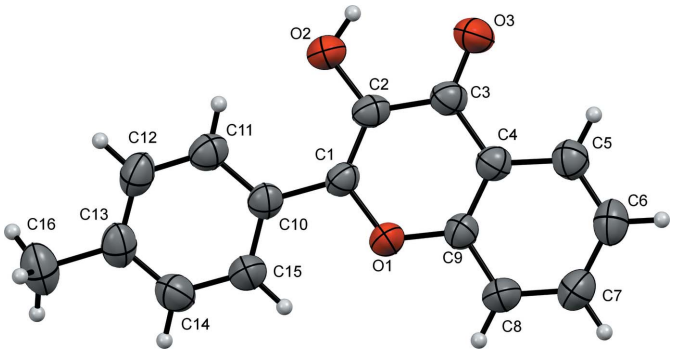



**Figure 1**
A view of the molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

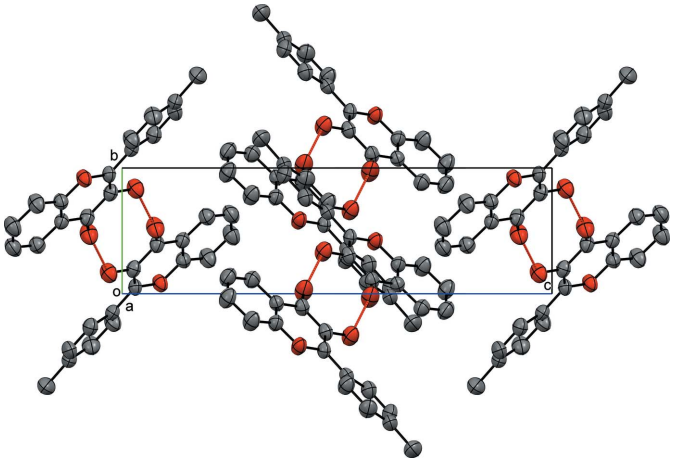



**Figure 2**
Crystal packing diagram of the title compound, viewed along the *a* axis. H atoms have been omitted for clarity and O···O bonds represent hydrogen-bonded O-atom sites.

chlorophenyl)-3-hydroxy-4*H*-chromen-4-one is nearly planar, with the phenyl ring tilted by 15.92 (8)° with respect to the benzopyranone ring (Zingales & Padgett, 2017), 3-hydroxy-2-(4-hydroxyphenyl)-4*H*-chromen-4-one, where the angle is 18.9 (4)° (Wera *et al.*, 2011*a*), and 3-hydroxy-2-(4-methoxyphenyl)-4*H*-chromen-4-one, where the corresponding angle is 12.3 (1)° (Wera *et al.*, 2011*b*). The crystal structure exhibits a classic herringbone pattern (Fig. 2) with the blocks consisting of the hydrogen-bonded dimers.

## Synthesis and crystallization

The title compound was synthesized (Fig. 3) by the aldol condensation of 2-hydroxyacetophenone and 4-methyl-

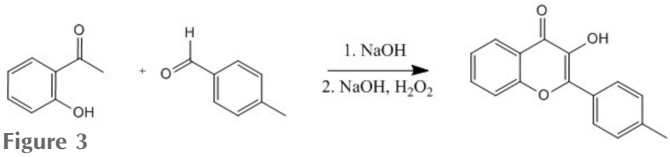



**Figure 3**
Synthesis of the title compound.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O3$^{i}$ | 0.88 (2) | 1.92 (2) | 2.721 (2) | 151 (3) |
| C11—H11···O2 | 0.93 | 2.24 | 2.838 (3) | 122 |

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

benzaldehyde to yield the chalcone (*E*)-1-(2-hydroxyphenyl)-3-(*p*-tolyl)prop-2-en-1-one, followed by its oxidative cyclization to the flavone, as reported in the literature (Kurzwernhart *et al.*, 2012). 2-Hydroxyacetophenone (4.8 g, 36 mmol) and 4-methylbenzaldehyde (4.3 g, 36 mmol) were dissolved in ethanol (90 ml). An NaOH solution (5 *M*, 30 ml) was added and the reaction was stirred until a precipitate formed. The reaction mixture was acidified to pH 6 with dilute acetic acid. The solids were filtered off and taken directly to the next step. (*E*)-1-(2-Hydroxyphenyl)-3-(*p*-tolyl)prop-2-en-1-one (3.5 g, 14 mmol) was then suspended in EtOH (30 ml) and cooled in an ice water bath. An NaOH solution (5 *M*, 5 ml) and $H_2O_2$ (30%, 2.2 equiv., 3 ml) were added and the reaction stirred overnight, warming to room temperature. The reaction mixture was acidified to pH 1 with HCl (6 *M*) and poured into cold water (400 ml). The white solid was collected by filtration and recrystallization of an MeOH solution afforded yellow

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{16}H_{12}O_3$ |
| $M_r$ | 252.26 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 293 |
| *a*, *b*, *c* (Å) | 13.2958 (13), 5.1981 (4), 18.8162 (15) |
| $\beta$ (°) | 109.212 (9) |
| $V$ (Å$^3$) | 1228.02 (19) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.09 |
| Crystal size (mm) | 0.50 × 0.20 × 0.05 |
| | |
| Data collection | |
| Diffractometer | Rigaku XtaLAB mini |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018) |
| $T_{min}$, $T_{max}$ | 0.838, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12529, 2252, 1394 |
| $R_{int}$ | 0.056 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.602 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.054, 0.170, 1.04 |
| No. of reflections | 2252 |
| No. of parameters | 176 |
| No. of restraints | 1 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.21, −0.20 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018*/3 (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

crystals (1.7 g, 19% yield over two steps). The structure was confirmed to match the literature (Kurzwernhart *et al.*, 2012). $^1$H NMR (300 MHz, $CDCl_3$, p.p.m.): $\delta$ 8.26 (*dd*, *J* = 1.2, 8.1 Hz, 1H, Ar—H), 8.17 (*d*, *J* = 8.2 Hz, 2H, Ar—H), 7.72 (*td*, *J* = 1.7, 8.6 Hz, 1H, Ar—H), 7.6 (*d*, *J* = 8.2 Hz, 1H, Ar—H), 7.42 (*t*, *J* = 7.6 Hz, 1H, Ar—H), 7.36 (*d*, *J* = 8.2 Hz, 2H, Ar—H), 7.01 (*bs*, 1H, OH), 2.45 (*s*, 3H, $CH_3$).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

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## References

Anderson, S. N., Richards, J. M., Esquer, H. J., Benninghoff, A. D., Arif, A. M. & Berreau, L. M. (2015). *ChemistryOpen*, **4**, 590–594.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Kurzwernhart, A., Kandioller, W., Bächler, S., Bartel, C., Martic, S., Buczkowska, M., Mühlgassner, G., Jakupec, M. A., Kraatz, H.-B., Bednarski, P. J., Arion, V. B., Marko, D., Keppler, B. K. & Hartinger, C. G. (2012). *J. Med. Chem.* **55**, 10512–10522.
Rigaku OD (2018). *CrysAlis PRO*. Oxford Diffraction/Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Wera, M., Pivovarenko, V. G. & Błażejowski, J. (2011*a*). *Acta Cryst.* E**67**, o264–o265.
Wera, M., Serdiuk, I. E., Roshal, A. D. & Błażejowski, J. (2011*b*). *Acta Cryst.* E**67**, o440.
Zingales, S. & Padgett, C. (2017). *IUCrData*, **2**, x170996.

# full crystallographic data

*IUCrData* (2018). **3**, x181138 [https://doi.org/10.1107/S2414314618011380]

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### 3-Hydroxy-2-(4-methylphenyl)-4*H*-chromen-4-one

*Crystal data*

$C_{16}H_{12}O_3$
$M_r$ = 252.26
Monoclinic, $P2_1/n$
$a$ = 13.2958 (13) Å
$b$ = 5.1981 (4) Å
$c$ = 18.8162 (15) Å
$\beta$ = 109.212 (9)°
$V$ = 1228.02 (19) Å$^3$
$Z$ = 4
$F(000)$ = 528
$D_x$ = 1.364 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 1203 reflections
$\theta$ = 2.3–21.8°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
Needle, yellow
0.50 × 0.20 × 0.05 mm

*Data collection*

Rigaku XtaLAB mini diffractometer
Radiation source: Sealed Tube, Rigaku (Mo) X-ray Source
Graphite Monochromator monochromator
Detector resolution: 13.6612 pixels mm$^{-1}$
profile data from $\omega$–scans
Absorption correction: multi-scan CrysAlisPro (Rigaku OD, 2018)
$T_{min}$ = 0.838, $T_{max}$ = 1.000
12529 measured reflections
2252 independent reflections
1394 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.056
$\theta_{max}$ = 25.3°, $\theta_{min}$ = 2.3°
$h$ = −15→16
$k$ = −5→6
$l$ = −22→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.170
$S$ = 1.04
2252 reflections
176 parameters
1 restraint
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0872P)^2 + 0.0826P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

*Special details*

**Refinement**. All C-bound H atoms were positioned geometrically and refined as riding, with C—H = 0.93 or 0.96 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) or $U_{iso}$(H) = 1.5$U_{eq}$(C) for C(H) and $CH_3$ groups, respectively. H atoms involved in O—H···O hydrogen bonds were located on a difference Fourier map and refined isotropically with $U_{iso}$(H) = 1.5$U_{eq}$(O). The H2—O2 distance was restrained to a target value of 0.84 (2) Å, using a DFIX command in *SHELXL* (Sheldrick, 2015*b*).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.64822 (13) | 0.5830 (3) | 0.41165 (9) | 0.0524 (5) |
| O2 | 0.92078 (14) | 0.6646 (4) | 0.53130 (10) | 0.0596 (5) |
| H2 | 0.965 (2) | 0.788 (5) | 0.5307 (17) | 0.089* |
| O3 | 0.90470 (15) | 1.0256 (4) | 0.42282 (10) | 0.0690 (6) |
| C1 | 0.74245 (18) | 0.5511 (4) | 0.46966 (12) | 0.0432 (6) |
| C2 | 0.82869 (18) | 0.6966 (5) | 0.47341 (13) | 0.0454 (6) |
| C3 | 0.82503 (19) | 0.8942 (5) | 0.41869 (13) | 0.0475 (6) |
| C4 | 0.72316 (19) | 0.9250 (4) | 0.35938 (13) | 0.0444 (6) |
| C5 | 0.7068 (2) | 1.1130 (5) | 0.30258 (14) | 0.0542 (7) |
| H5 | 0.761741 | 1.224393 | 0.303120 | 0.065* |
| C6 | 0.6103 (2) | 1.1322 (5) | 0.24672 (15) | 0.0633 (8) |
| H6 | 0.599902 | 1.256239 | 0.209369 | 0.076* |
| C7 | 0.5278 (2) | 0.9665 (6) | 0.24576 (16) | 0.0652 (8) |
| H7 | 0.462708 | 0.979595 | 0.207336 | 0.078* |
| C8 | 0.5412 (2) | 0.7834 (5) | 0.30083 (14) | 0.0609 (8) |
| H8 | 0.485876 | 0.672806 | 0.300054 | 0.073* |
| C9 | 0.6391 (2) | 0.7672 (5) | 0.35765 (13) | 0.0474 (6) |
| C10 | 0.73289 (19) | 0.3510 (4) | 0.52236 (12) | 0.0448 (6) |
| C11 | 0.8214 (2) | 0.2358 (5) | 0.57398 (13) | 0.0537 (7) |
| H11 | 0.889464 | 0.284054 | 0.575491 | 0.064* |
| C12 | 0.8091 (2) | 0.0512 (5) | 0.62279 (15) | 0.0601 (7) |
| H12 | 0.869413 | −0.024043 | 0.656593 | 0.072* |
| C13 | 0.7094 (2) | −0.0264 (5) | 0.62317 (14) | 0.0569 (7) |
| C14 | 0.6227 (2) | 0.0887 (5) | 0.57241 (15) | 0.0641 (8) |
| H14 | 0.555015 | 0.041315 | 0.571865 | 0.077* |
| C15 | 0.6321 (2) | 0.2730 (5) | 0.52190 (15) | 0.0599 (7) |
| H15 | 0.571313 | 0.344940 | 0.487657 | 0.072* |
| C16 | 0.6976 (3) | −0.2350 (6) | 0.67638 (15) | 0.0745 (9) |
| H16A | 0.709676 | −0.400200 | 0.657852 | 0.112* |
| H16B | 0.626982 | −0.229299 | 0.679462 | 0.112* |
| H16C | 0.748656 | −0.207334 | 0.725449 | 0.112* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0470 (10) | 0.0573 (11) | 0.0434 (10) | −0.0100 (8) | 0.0021 (8) | 0.0074 (8) |
| O2 | 0.0438 (11) | 0.0700 (13) | 0.0563 (11) | −0.0092 (9) | 0.0045 (9) | 0.0091 (10) |
| O3 | 0.0565 (12) | 0.0855 (14) | 0.0582 (12) | −0.0253 (11) | 0.0099 (9) | 0.0103 (10) |
| C1 | 0.0399 (14) | 0.0497 (14) | 0.0345 (12) | −0.0004 (11) | 0.0048 (10) | −0.0002 (10) |
| C2 | 0.0389 (14) | 0.0545 (15) | 0.0399 (13) | −0.0022 (11) | 0.0089 (11) | −0.0050 (11) |
| C3 | 0.0456 (15) | 0.0565 (16) | 0.0393 (13) | −0.0089 (12) | 0.0123 (12) | −0.0036 (11) |
| C4 | 0.0466 (14) | 0.0485 (14) | 0.0374 (13) | −0.0045 (11) | 0.0130 (11) | −0.0046 (10) |
| C5 | 0.0595 (17) | 0.0555 (16) | 0.0478 (15) | −0.0037 (13) | 0.0179 (14) | 0.0028 (12) |
| C6 | 0.074 (2) | 0.0633 (18) | 0.0525 (17) | 0.0055 (15) | 0.0211 (16) | 0.0145 (13) |
| C7 | 0.0559 (18) | 0.077 (2) | 0.0538 (16) | 0.0015 (15) | 0.0057 (14) | 0.0140 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C8 | 0.0465 (16) | 0.0712 (18) | 0.0551 (16) | −0.0122 (13) | 0.0032 (13) | 0.0087 (14) |
| C9 | 0.0491 (15) | 0.0487 (14) | 0.0401 (13) | −0.0023 (12) | 0.0089 (11) | 0.0040 (11) |
| C10 | 0.0508 (15) | 0.0422 (13) | 0.0368 (13) | −0.0047 (11) | 0.0082 (11) | −0.0039 (10) |
| C11 | 0.0517 (16) | 0.0588 (16) | 0.0445 (14) | −0.0024 (13) | 0.0077 (12) | −0.0025 (12) |
| C12 | 0.0697 (19) | 0.0577 (17) | 0.0427 (14) | 0.0055 (14) | 0.0047 (13) | 0.0064 (12) |
| C13 | 0.081 (2) | 0.0459 (15) | 0.0391 (14) | −0.0079 (14) | 0.0129 (14) | −0.0024 (11) |
| C14 | 0.0619 (19) | 0.0672 (18) | 0.0596 (17) | −0.0179 (14) | 0.0153 (15) | 0.0034 (14) |
| C15 | 0.0508 (16) | 0.0649 (18) | 0.0542 (15) | −0.0108 (14) | 0.0042 (12) | 0.0100 (13) |
| C16 | 0.110 (3) | 0.0560 (18) | 0.0596 (18) | −0.0103 (17) | 0.0310 (18) | 0.0045 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C9 | 1.372 (3) | C8—C9 | 1.389 (3) |
| O1—C1 | 1.374 (3) | C8—H8 | 0.9300 |
| O2—C2 | 1.355 (3) | C10—C11 | 1.391 (3) |
| O2—H2 | 0.878 (18) | C10—C15 | 1.398 (4) |
| O3—C3 | 1.241 (3) | C11—C12 | 1.375 (4) |
| C1—C2 | 1.356 (3) | C11—H11 | 0.9300 |
| C1—C10 | 1.471 (3) | C12—C13 | 1.387 (4) |
| C2—C3 | 1.444 (3) | C12—H12 | 0.9300 |
| C3—C4 | 1.453 (3) | C13—C14 | 1.369 (4) |
| C4—C9 | 1.378 (3) | C13—C16 | 1.518 (4) |
| C4—C5 | 1.411 (3) | C14—C15 | 1.384 (4) |
| C5—C6 | 1.368 (4) | C14—H14 | 0.9300 |
| C5—H5 | 0.9300 | C15—H15 | 0.9300 |
| C6—C7 | 1.390 (4) | C16—H16A | 0.9600 |
| C6—H6 | 0.9300 | C16—H16B | 0.9600 |
| C7—C8 | 1.375 (4) | C16—H16C | 0.9600 |
| C7—H7 | 0.9300 | | |
| | | | |
| C9—O1—C1 | 120.49 (18) | O1—C9—C8 | 116.4 (2) |
| C2—O2—H2 | 110 (2) | C4—C9—C8 | 122.0 (2) |
| C2—C1—O1 | 120.6 (2) | C11—C10—C15 | 118.0 (2) |
| C2—C1—C10 | 128.2 (2) | C11—C10—C1 | 122.3 (2) |
| O1—C1—C10 | 111.23 (19) | C15—C10—C1 | 119.8 (2) |
| O2—C2—C1 | 119.9 (2) | C12—C11—C10 | 120.5 (3) |
| O2—C2—C3 | 118.0 (2) | C12—C11—H11 | 119.8 |
| C1—C2—C3 | 122.0 (2) | C10—C11—H11 | 119.8 |
| O3—C3—C2 | 121.3 (2) | C11—C12—C13 | 122.0 (3) |
| O3—C3—C4 | 123.3 (2) | C11—C12—H12 | 119.0 |
| C2—C3—C4 | 115.5 (2) | C13—C12—H12 | 119.0 |
| C9—C4—C5 | 118.2 (2) | C14—C13—C12 | 117.1 (2) |
| C9—C4—C3 | 119.8 (2) | C14—C13—C16 | 121.7 (3) |
| C5—C4—C3 | 122.0 (2) | C12—C13—C16 | 121.1 (3) |
| C6—C5—C4 | 120.3 (2) | C13—C14—C15 | 122.4 (3) |
| C6—C5—H5 | 119.9 | C13—C14—H14 | 118.8 |
| C4—C5—H5 | 119.9 | C15—C14—H14 | 118.8 |
| C5—C6—C7 | 120.1 (2) | C14—C15—C10 | 120.0 (3) |

| | | | |
|---|---|---|---|
| C5—C6—H6 | 120.0 | C14—C15—H15 | 120.0 |
| C7—C6—H6 | 120.0 | C10—C15—H15 | 120.0 |
| C8—C7—C6 | 120.9 (3) | C13—C16—H16A | 109.5 |
| C8—C7—H7 | 119.6 | C13—C16—H16B | 109.5 |
| C6—C7—H7 | 119.6 | H16A—C16—H16B | 109.5 |
| C7—C8—C9 | 118.6 (2) | C13—C16—H16C | 109.5 |
| C7—C8—H8 | 120.7 | H16A—C16—H16C | 109.5 |
| C9—C8—H8 | 120.7 | H16B—C16—H16C | 109.5 |
| O1—C9—C4 | 121.6 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O3$^{i}$ | 0.88 (2) | 1.92 (2) | 2.721 (2) | 151 (3) |
| C11—H11···O2 | 0.93 | 2.24 | 2.838 (3) | 122 |

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+1.