# Crystal structure of 6,6'-dimethyl-2H,2'H-3,4'-bichromene-2,2'-dione
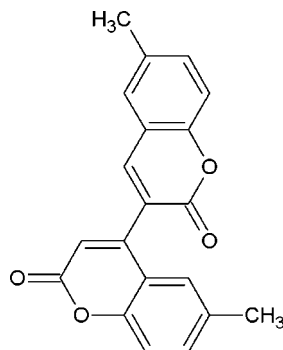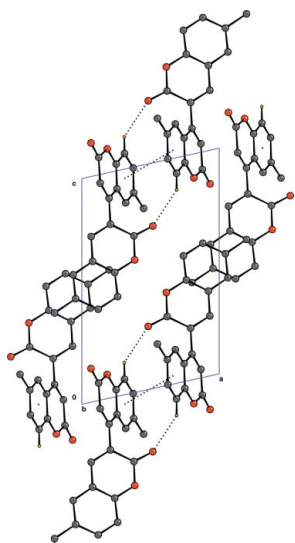
Kiran K. Pujar,[a] Manohar V. Kulkarni[a]* and G. N. Anil Kumar[b]

[a]Department of Chemistry, Karnatak University, Dharwad 580 010, India, and [b]Department of Physics, M S Ramaiah Institute of Technology, MSRIT Post, Bangalore 560 054, India. *Correspondence e-mail: anilgn@msrit.edu

In the title compound, $C_{20}H_{14}O_4$, the dihedral angle between the two coumarin ring systems is 52.37 (19)°, showing a *gauche* arrangement across the C—C bond which links the two units. The carbonyl groups of the two coumarin units adopt an s-*trans* arrangement. In the crystal, pairs of C—H···O hydrogen bonds and π–π interactions [centroid–centroid distance = 3.631 (2) Å] connect the molecules into inversion dimers.

## 1. Chemical context

Bicoumarins, in which two coumarin ring systems are directly linked through a C—C bond, are a group of regio-isomers which are of synthetic interest (Ilyas & Parveen, 1996; Dubovik *et al.*, 2004; Frasinyuk *et al.*, 2012). Their natural occurrence and structural diversity originate from various positions of the linkage which can lead to pyran–pyran-linked bicoumarins, *viz.*, 3-3', 3-4', 4-4', or pyran–benzene-linked bicoumarins wherein the points of linkage are C3/C4 with the C5–C8 positions in the second coumarin moiety (Hussain *et al.*, 2012). 3-3' Bicoumarins isolated from Chinese medicinal plants and Mediterranean sponges (Panichayupakaranant *et al.*, 1998) have been shown to exhibit insecticidal and anti-proliferative properties. 8-8' Bicoumarins have shown anti-leukemic, nematocidal and cardiotoxic activity as well as antischistosomial, sedative and hypotensive effects (Ulubelen *et al.*, 1986). 6-8' Bicoumarins have been evaluated for urease inhibitory activity (Ayaz *et al.*, 2006). Atropisomerism has been observed for naturally occurring 3-6' bicoumarins (Zhan *et al.*, 2003). 5-5' Bicoumarins competitively inhibit epoxide reductase of vitamin K, preventing the reduction of vitamin K into hydroquinone, leading to their anticoagulant activity (Zhou *et al.*, 2009). 3-8' Bicoumarins exhibit cytotoxicity towards human solid tumour cell lines, affording $ED_{50}$ values of 7.5, 55, 5.8 µg/ml against non-small-cell-lung carcinoma A-549, breast adenocarcinoma MCF-7, and colon adeno-carcinoma HT-29 cells respectively (Tepaske & Gloer, 1992).
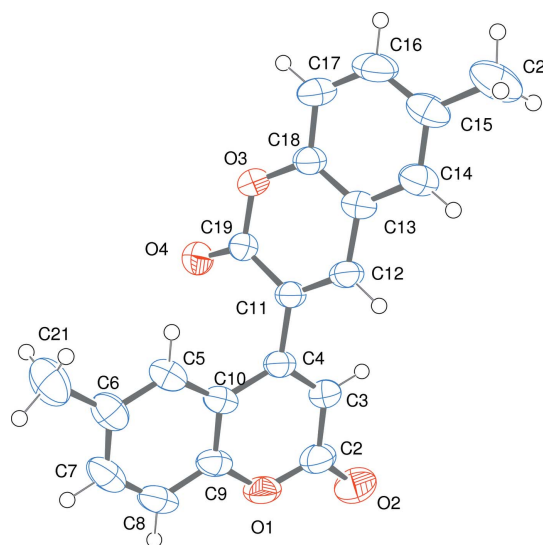
**Figure 1**
The molecular structure of the title compound, showing the atom-labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

In view of the above cited activities of directly linked coumarin dimers, the present work reports the synthesis under metal-free conditions of a new 4-3′ bicoumarin and its structure.

## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The packing viewed along the *b* axis (Fig. 2) shows the existence of intermolecular C—H···O hydrogen bonds between the carbonyl O4 of one coumarin moiety and the aromatic H8 of the second unit (Table 1), which has also been observed in a 3-5′ bicoumarin (Fun *et al.*, 2009). The two coumarin rings exhibit an *s-trans* arrangement across the C4—C11 bond for the two double bonds *viz*. C3≡C4 and C11≡C12. The non-planar nature of the bi-heterocyclic system is revealed through the torsion angles C3—C4—C11—C12 [−52.37 (19)°] and C10—C4—C11—C19 [−59.32 (17)°], which almost corresponds to a *gauche* conformation.

## 3. Supramolecular features

In the crystal, pairs of C—H···O hydrogen bonds and π–π interactions [$Cg1···Cg1^i$ = 3.631 (2); slippage = 1.491 Å; $Cg1$ is the centroid of the C5–C10 ring; symmetry code: (i) 1 − x, −y, −z] connect molecules into inversion dimers (Fig. 2).

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

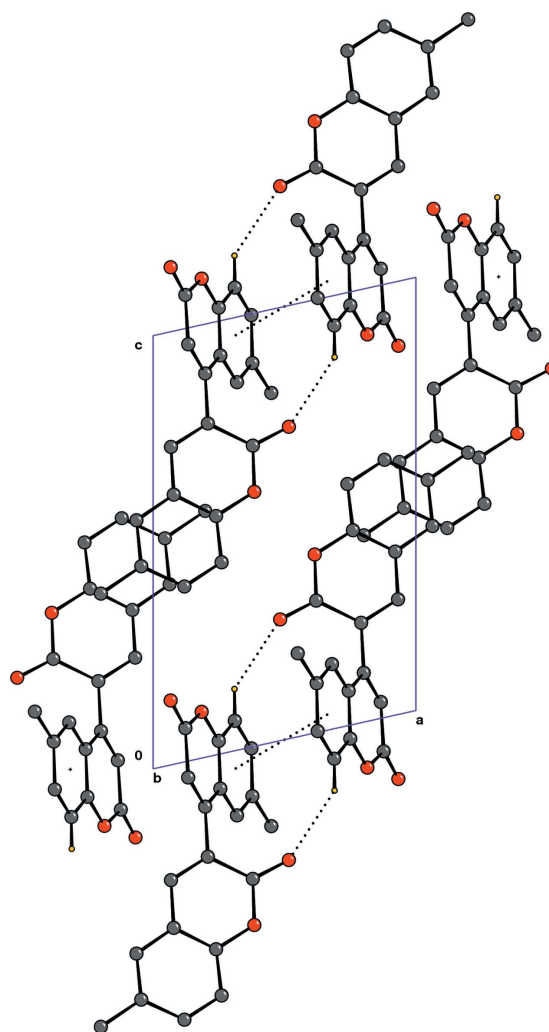| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C8—H8···O4$^i$ | 0.93 | 2.53 | 3.330 (2) | 145 |

Symmetry code: (i) −x + 1, −y, −z.



**Figure 2**
A packing diagram of the title compound, viewed along the *b* axis. Dashed lines indicate C—H···O hydrogen bonds and π–π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.35, updates Feb 2014; Groom & Allen, 2014) revealed two related structures, *viz.* 7,7′,8,8′-tetramethoxy-4,4′-dimethyl-3,5′-bichromene-2,2′-dione (Fun *et al.*, 2009) and 7,7′-dihydroxy-4,4′-dimethyl-3,4-dihydro-2*H*,2′*H*-4,6′-bichromene-2,2′-dione (Pereira Silva *et al.*, 2011). In these two compounds, the dihedral angles between the coumarin ring systems are 79.93 (3) and 88.07 (2)°, respectively. The corresponding angle in the title compound is 52.37 (19)°.

## 5. Synthesis and Crystallization

6-Methylcoumarin 4-acetic acid (0.01 mol) and 5-methyl-salicylaldehyde (0.01 mol) were taken in a round-bottomed flask containing (1.5 eq) NaH and 3 ml of acetic anhydride. The flask, fitted with a guard tube, was stirred for 1.5 h. The progress of the reaction was monitored by TLC, the solid that separated was filtered off and washed with diethyl ether and

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{20}H_{14}O_4$ |
| $M_r$ | 318.31 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 296 |
| $a, b, c$ (Å) | 7.834 (1), 8.0455 (9), 12.7952 (15) |
| $\alpha, \beta, \gamma$ (°) | 79.492 (5), 77.096 (4), 86.637 (5) |
| $V$ (Å$^3$) | 772.78 (16) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.10 |
| Crystal size (mm) | $0.35 \times 0.31 \times 0.25$ |
| | |
| Data collection | |
| Diffractometer | Bruker *SMART* CCD area-detector |
| Absorption correction | Multi-scan (*SADABS*; Sheldrick, 1996) |
| $T_{min}, T_{max}$ | 0.954, 0.964 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12862, 3499, 2509 |
| $R_{int}$ | 0.027 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.648 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.046, 0.140, 1.05 |
| No. of reflections | 3499 |
| No. of parameters | 219 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å$^{-3}$) | 0.19, −0.20 |

Computer programs: *SMART* and *SAINT* (Bruker, 1998), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *CAMERON* (Watkin *et al.*, 1996), *PARST* (Nardelli, 1996) and *PLATON* (Spek, 2009).

again with 5% $NaHCO_3$ to remove unreacted 6-methyl-coumarin 4-acetic acid. Then the solid was dried and recrystallized from ethanol. Crystals suitable for diffraction studies were obtained through slow evaporation from a DMF solution.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

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# Crystal structure of 6,6′-dimethyl-2*H*,2′*H*-3,4′-bichromene-2,2′-dione

**Kiran K. Pujar, Manohar V. Kulkarni and G. N. Anil Kumar**

## Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *PARST* (Nardelli, 1996) and *PLATON* (Spek, 2009).

### 6,6′-Dimethyl-2*H*,2′*H*-3,4′-bichromene-2,2′-dione

*Crystal data*

| | |
|---|---|
| $C_{20}H_{14}O_4$ | $Z = 2$ |
| $M_r = 318.31$ | $F(000) = 332$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.368$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 7.834$ (1) Å | Cell parameters from 560 reflections |
| $b = 8.0455$ (9) Å | $\theta = 1.7°$ |
| $c = 12.7952$ (15) Å | $\mu = 0.10$ mm$^{-1}$ |
| $\alpha = 79.492$ (5)° | $T = 296$ K |
| $\beta = 77.096$ (4)° | Block, white |
| $\gamma = 86.637$ (5)° | $0.35 \times 0.31 \times 0.25$ mm |
| $V = 772.78$ (16) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 12862 measured reflections |
| Radiation source: fine-focus sealed tube | 3499 independent reflections |
| Graphite monochromator | 2509 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.027$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 27.4°$, $\theta_{min} = 1.7°$ |
| $T_{min} = 0.954$, $T_{max} = 0.964$ | $h = -10 \rightarrow 10$ |
| | $k = -10 \rightarrow 9$ |
| | $l = -16 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.046$ | |
| $wR(F^2) = 0.140$ | H-atom parameters constrained |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.1433P]$ |
| 3499 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 219 parameters | $(\Delta/\sigma)_{max} < 0.001$ |
| 0 restraints | $\Delta\rho_{max} = 0.19$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{min} = -0.20$ e Å$^{-3}$ |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

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

|  | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.81516 (14) | 0.16314 (15) | −0.10679 (8) | 0.0577 (3) |
| O2 | 0.9332 (2) | 0.4150 (2) | −0.14906 (10) | 0.0853 (4) |
| O3 | 0.61479 (14) | 0.15867 (15) | 0.41223 (8) | 0.0569 (3) |
| O4 | 0.48324 (15) | 0.13864 (15) | 0.27995 (9) | 0.0603 (3) |
| C2 | 0.8773 (2) | 0.2996 (2) | −0.07754 (13) | 0.0583 (4) |
| C3 | 0.8662 (2) | 0.2942 (2) | 0.03783 (11) | 0.0508 (4) |
| H3 | 0.9052 | 0.3863 | 0.06 | 0.061* |
| C4 | 0.80175 (18) | 0.16160 (17) | 0.11386 (11) | 0.0405 (3) |
| C5 | 0.6808 (2) | −0.13246 (17) | 0.15031 (12) | 0.0478 (4) |
| H5 | 0.6783 | −0.1418 | 0.2242 | 0.057* |
| C6 | 0.6220 (2) | −0.26560 (18) | 0.11392 (14) | 0.0547 (4) |
| C7 | 0.6262 (2) | −0.2483 (2) | 0.00295 (15) | 0.0595 (5) |
| H7 | 0.5852 | −0.3356 | −0.0229 | 0.071* |
| C8 | 0.6891 (2) | −0.1057 (2) | −0.06922 (13) | 0.0560 (4) |
| H8 | 0.6905 | −0.0967 | −0.1429 | 0.067* |
| C9 | 0.75025 (18) | 0.0239 (2) | −0.03095 (12) | 0.0460 (4) |
| C10 | 0.74384 (18) | 0.01530 (17) | 0.08010 (11) | 0.0414 (3) |
| C11 | 0.79180 (18) | 0.16893 (16) | 0.23068 (10) | 0.0386 (3) |
| C12 | 0.93182 (19) | 0.20659 (19) | 0.26592 (11) | 0.0450 (3) |
| H12 | 1.0386 | 0.2245 | 0.2165 | 0.054* |
| C13 | 0.92131 (19) | 0.21999 (17) | 0.37755 (11) | 0.0433 (3) |
| C14 | 1.0631 (2) | 0.2583 (2) | 0.41766 (13) | 0.0540 (4) |
| H14 | 1.1719 | 0.277 | 0.3705 | 0.065* |
| C15 | 1.0449 (2) | 0.2688 (2) | 0.52638 (13) | 0.0572 (4) |
| C16 | 0.8808 (3) | 0.2377 (2) | 0.59489 (13) | 0.0679 (5) |
| H16 | 0.8669 | 0.2432 | 0.6683 | 0.081* |
| C17 | 0.7393 (3) | 0.1995 (2) | 0.55805 (13) | 0.0680 (5) |
| H17 | 0.6312 | 0.1788 | 0.6056 | 0.082* |
| C18 | 0.7602 (2) | 0.19221 (18) | 0.44840 (11) | 0.0472 (4) |
| C19 | 0.6205 (2) | 0.15326 (17) | 0.30488 (11) | 0.0440 (3) |
| C20 | 1.1984 (3) | 0.3134 (3) | 0.56865 (17) | 0.0830 (6) |
| H20A | 1.2798 | 0.2195 | 0.5708 | 0.124* |
| H20B | 1.1575 | 0.3386 | 0.6407 | 0.124* |
| H20C | 1.2554 | 0.4103 | 0.5214 | 0.124* |
| C21 | 0.5504 (3) | −0.4212 (2) | 0.19269 (18) | 0.0784 (6) |

| | | | |
|---|---|---|---|
| H21A | 0.6207 | −0.4505 | 0.2462 | 0.118* |
| H21B | 0.5529 | −0.5131 | 0.1539 | 0.118* |
| H21C | 0.4319 | −0.3991 | 0.2282 | 0.118* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0565 (7) | 0.0856 (8) | 0.0318 (5) | −0.0030 (6) | −0.0070 (5) | −0.0147 (5) |
| O2 | 0.1050 (11) | 0.1025 (10) | 0.0394 (6) | −0.0284 (8) | −0.0057 (7) | 0.0071 (7) |
| O3 | 0.0581 (7) | 0.0744 (7) | 0.0360 (5) | −0.0229 (5) | 0.0050 (5) | −0.0154 (5) |
| O4 | 0.0469 (7) | 0.0795 (8) | 0.0575 (7) | −0.0158 (6) | −0.0036 (5) | −0.0243 (6) |
| C2 | 0.0556 (10) | 0.0799 (11) | 0.0365 (8) | −0.0071 (8) | −0.0048 (7) | −0.0074 (8) |
| C3 | 0.0521 (9) | 0.0634 (9) | 0.0358 (7) | −0.0107 (7) | −0.0039 (7) | −0.0101 (7) |
| C4 | 0.0378 (7) | 0.0510 (8) | 0.0335 (7) | 0.0029 (6) | −0.0065 (6) | −0.0118 (6) |
| C5 | 0.0586 (9) | 0.0446 (7) | 0.0461 (8) | 0.0105 (6) | −0.0207 (7) | −0.0154 (6) |
| C6 | 0.0581 (10) | 0.0444 (8) | 0.0694 (10) | 0.0120 (7) | −0.0236 (8) | −0.0224 (7) |
| C7 | 0.0564 (10) | 0.0631 (10) | 0.0734 (11) | 0.0133 (8) | −0.0241 (9) | −0.0415 (9) |
| C8 | 0.0469 (9) | 0.0817 (11) | 0.0496 (9) | 0.0154 (8) | −0.0155 (7) | −0.0367 (8) |
| C9 | 0.0380 (8) | 0.0641 (9) | 0.0394 (7) | 0.0111 (6) | −0.0098 (6) | −0.0204 (7) |
| C10 | 0.0409 (8) | 0.0496 (8) | 0.0377 (7) | 0.0100 (6) | −0.0129 (6) | −0.0162 (6) |
| C11 | 0.0453 (8) | 0.0393 (6) | 0.0306 (6) | −0.0017 (5) | −0.0050 (6) | −0.0079 (5) |
| C12 | 0.0421 (8) | 0.0590 (8) | 0.0336 (7) | 0.0011 (6) | −0.0030 (6) | −0.0146 (6) |
| C13 | 0.0521 (9) | 0.0452 (7) | 0.0338 (7) | 0.0034 (6) | −0.0103 (6) | −0.0105 (6) |
| C14 | 0.0546 (10) | 0.0674 (10) | 0.0456 (8) | 0.0091 (7) | −0.0174 (7) | −0.0195 (7) |
| C15 | 0.0792 (12) | 0.0534 (9) | 0.0477 (9) | 0.0131 (8) | −0.0316 (9) | −0.0139 (7) |
| C16 | 0.1023 (15) | 0.0711 (11) | 0.0322 (8) | −0.0038 (10) | −0.0178 (9) | −0.0092 (7) |
| C17 | 0.0863 (13) | 0.0816 (12) | 0.0322 (8) | −0.0220 (10) | 0.0009 (8) | −0.0106 (8) |
| C18 | 0.0623 (10) | 0.0451 (7) | 0.0328 (7) | −0.0093 (7) | −0.0048 (7) | −0.0074 (6) |
| C19 | 0.0517 (9) | 0.0426 (7) | 0.0367 (7) | −0.0106 (6) | −0.0025 (6) | −0.0101 (6) |
| C20 | 0.0974 (15) | 0.1004 (15) | 0.0710 (12) | 0.0216 (12) | −0.0535 (12) | −0.0306 (11) |
| C21 | 0.1041 (16) | 0.0426 (8) | 0.0973 (15) | 0.0001 (9) | −0.0352 (12) | −0.0189 (9) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C2 | 1.370 (2) | C11—C12 | 1.345 (2) |
| O1—C9 | 1.3805 (19) | C11—C19 | 1.458 (2) |
| O2—C2 | 1.204 (2) | C12—C13 | 1.4358 (18) |
| O3—C19 | 1.3728 (17) | C12—H12 | 0.93 |
| O3—C18 | 1.3793 (18) | C13—C18 | 1.383 (2) |
| O4—C19 | 1.2055 (18) | C13—C14 | 1.394 (2) |
| C2—C3 | 1.452 (2) | C14—C15 | 1.384 (2) |
| C3—C4 | 1.344 (2) | C14—H14 | 0.93 |
| C3—H3 | 0.93 | C15—C16 | 1.392 (3) |
| C4—C10 | 1.4538 (18) | C15—C20 | 1.509 (2) |
| C4—C11 | 1.4911 (17) | C16—C17 | 1.368 (3) |
| C5—C6 | 1.383 (2) | C16—H16 | 0.93 |
| C5—C10 | 1.395 (2) | C17—C18 | 1.387 (2) |
| C5—H5 | 0.93 | C17—H17 | 0.93 |

| | | | |
|---|---|---|---|
| C6—C7 | 1.394 (2) | C20—H20A | 0.96 |
| C6—C21 | 1.506 (2) | C20—H20B | 0.96 |
| C7—C8 | 1.374 (2) | C20—H20C | 0.96 |
| C7—H7 | 0.93 | C21—H21A | 0.96 |
| C8—C9 | 1.381 (2) | C21—H21B | 0.96 |
| C8—H8 | 0.93 | C21—H21C | 0.96 |
| C9—C10 | 1.3997 (18) | | |
| | | | |
| C2—O1—C9 | 121.88 (12) | C13—C12—H12 | 119 |
| C19—O3—C18 | 122.41 (11) | C18—C13—C14 | 118.92 (13) |
| O2—C2—O1 | 117.52 (15) | C18—C13—C12 | 117.22 (13) |
| O2—C2—C3 | 125.51 (17) | C14—C13—C12 | 123.86 (14) |
| O1—C2—C3 | 116.95 (14) | C15—C14—C13 | 121.18 (16) |
| C4—C3—C2 | 122.65 (14) | C15—C14—H14 | 119.4 |
| C4—C3—H3 | 118.7 | C13—C14—H14 | 119.4 |
| C2—C3—H3 | 118.7 | C14—C15—C16 | 117.86 (15) |
| C3—C4—C10 | 119.22 (12) | C14—C15—C20 | 120.80 (17) |
| C3—C4—C11 | 118.88 (12) | C16—C15—C20 | 121.34 (16) |
| C10—C4—C11 | 121.90 (12) | C17—C16—C15 | 122.34 (15) |
| C6—C5—C10 | 122.28 (14) | C17—C16—H16 | 118.8 |
| C6—C5—H5 | 118.9 | C15—C16—H16 | 118.8 |
| C10—C5—H5 | 118.9 | C16—C17—C18 | 118.71 (16) |
| C5—C6—C7 | 117.80 (15) | C16—C17—H17 | 120.6 |
| C5—C6—C21 | 120.70 (15) | C18—C17—H17 | 120.6 |
| C7—C6—C21 | 121.46 (15) | O3—C18—C13 | 121.18 (12) |
| C8—C7—C6 | 121.81 (14) | O3—C18—C17 | 117.84 (14) |
| C8—C7—H7 | 119.1 | C13—C18—C17 | 120.98 (15) |
| C6—C7—H7 | 119.1 | O4—C19—O3 | 117.19 (13) |
| C7—C8—C9 | 119.16 (14) | O4—C19—C11 | 125.75 (13) |
| C7—C8—H8 | 120.4 | O3—C19—C11 | 117.05 (13) |
| C9—C8—H8 | 120.4 | C15—C20—H20A | 109.5 |
| C8—C9—O1 | 117.05 (13) | C15—C20—H20B | 109.5 |
| C8—C9—C10 | 121.36 (15) | H20A—C20—H20B | 109.5 |
| O1—C9—C10 | 121.58 (13) | C15—C20—H20C | 109.5 |
| C5—C10—C9 | 117.54 (13) | H20A—C20—H20C | 109.5 |
| C5—C10—C4 | 124.84 (12) | H20B—C20—H20C | 109.5 |
| C9—C10—C4 | 117.62 (13) | C6—C21—H21A | 109.5 |
| C12—C11—C19 | 119.82 (12) | C6—C21—H21B | 109.5 |
| C12—C11—C4 | 121.73 (12) | H21A—C21—H21B | 109.5 |
| C19—C11—C4 | 118.09 (12) | C6—C21—H21C | 109.5 |
| C11—C12—C13 | 121.94 (13) | H21A—C21—H21C | 109.5 |
| C11—C12—H12 | 119 | H21B—C21—H21C | 109.5 |
| | | | |
| C9—O1—C2—O2 | 179.27 (14) | C3—C4—C11—C19 | 120.68 (15) |
| C9—O1—C2—C3 | −2.2 (2) | C10—C4—C11—C19 | −59.32 (17) |
| O2—C2—C3—C4 | 179.75 (17) | C19—C11—C12—C13 | 4.7 (2) |
| O1—C2—C3—C4 | 1.3 (2) | C4—C11—C12—C13 | 177.64 (12) |
| C2—C3—C4—C10 | 1.3 (2) | C11—C12—C13—C18 | 0.1 (2) |

| C2—C3—C4—C11 | −178.68 (14) | C11—C12—C13—C14 | 179.81 (13) |
| C10—C5—C6—C7 | −0.4 (2) | C18—C13—C14—C15 | −0.1 (2) |
| C10—C5—C6—C21 | −178.33 (15) | C12—C13—C14—C15 | −179.77 (14) |
| C5—C6—C7—C8 | 1.2 (2) | C13—C14—C15—C16 | 0.9 (2) |
| C21—C6—C7—C8 | 179.09 (15) | C13—C14—C15—C20 | −178.91 (15) |
| C6—C7—C8—C9 | 0.1 (2) | C14—C15—C16—C17 | −0.7 (3) |
| C7—C8—C9—O1 | 178.84 (13) | C20—C15—C16—C17 | 179.08 (17) |
| C7—C8—C9—C10 | −2.2 (2) | C15—C16—C17—C18 | −0.3 (3) |
| C2—O1—C9—C8 | 179.28 (14) | C19—O3—C18—C13 | −0.9 (2) |
| C2—O1—C9—C10 | 0.3 (2) | C19—O3—C18—C17 | 178.21 (14) |
| C6—C5—C10—C9 | −1.6 (2) | C14—C13—C18—O3 | 178.15 (13) |
| C6—C5—C10—C4 | 177.80 (13) | C12—C13—C18—O3 | −2.1 (2) |
| C8—C9—C10—C5 | 2.9 (2) | C14—C13—C18—C17 | −1.0 (2) |
| O1—C9—C10—C5 | −178.19 (12) | C12—C13—C18—C17 | 178.77 (14) |
| C8—C9—C10—C4 | −176.54 (13) | C16—C17—C18—O3 | −178.01 (15) |
| O1—C9—C10—C4 | 2.4 (2) | C16—C17—C18—C13 | 1.1 (3) |
| C3—C4—C10—C5 | 177.47 (13) | C18—O3—C19—O4 | −173.26 (13) |
| C11—C4—C10—C5 | −2.5 (2) | C18—O3—C19—C11 | 5.6 (2) |
| C3—C4—C10—C9 | −3.1 (2) | C12—C11—C19—O4 | 171.31 (14) |
| C11—C4—C10—C9 | 176.86 (12) | C4—C11—C19—O4 | −1.9 (2) |
| C3—C4—C11—C12 | −52.37 (19) | C12—C11—C19—O3 | −7.45 (19) |
| C10—C4—C11—C12 | 127.63 (15) | C4—C11—C19—O3 | 179.36 (11) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C8—H8···O4[i] | 0.93 | 2.53 | 3.330 (2) | 145 |

Symmetry code: (i) −x+1, −y, −z.