Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Diospyrin

**William T. A. Harrison* and Oliver C. Musgrave**

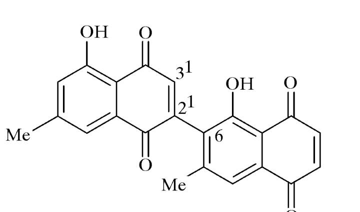
Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

Received 4 March 2004
Accepted 31 March 2004
Online 11 May 2004

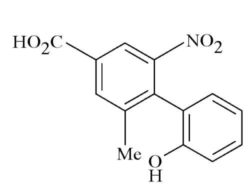
The structure of the title natural product, 1′,5-dihydroxy-3′,7-dimethyl-2,2′-binaphthalene-1,4,5′,8′-tetrone, $C_{22}H_{14}O_6$, confirms the atomic connectivity postulated on the basis of spectroscopic data. The geometric parameters are normal and the angle between the planes of the two ring systems is 59.74 (2)°. The crystal packing is influenced by O—H···O hydrogen bonds, and possible short C—H···O and π–π stacking interactions.

## Comment

Diopyrin, $C_{22}H_{14}O_6$, (I), is an orange–red naphthoquinonyl-naphthoquinone that is present in the heartwood of many species of Diospyros (persimmon) trees (Thomson, 1987). The potent antimycobacterial properties of diospyrin and its analogues have been investigated by various workers (Lall *et al.*, 2003, and references therein). Arguments based on NMR spectra (Sidhu & Pardhasaradhi, 1967, 1970; Lillie & Musgrave, 1977) indicated that diospyrin has the structure shown in the scheme below, with a 6-2[1] linkage present between the naphthoquinonyl units, and a recent synthesis (Yoshida & Mori, 2000) has provided support for this hypothesis. However, the alternative 6-3[1] mode of linkage has never been conclusively disproved. We have now established crystallographically that diospyrin does indeed have the 6-2[1] structure (Fig. 1).




(I)




(II)

The geometric parameters for (I) (Table 1) are consistent with those reported for other naphthoquinone systems (Lynch & McClenaghan, 2002). In the crystal, the two ring systems (C1–C11/O1–O3, with an r.m.s. deviation from the least-squares plane of 0.048 Å, and C12–C22/O5/O6, with an r.m.s. deviation of 0.069 Å) are not coplanar, the angle between their least-squares planes being 59.74 (2)°. The length of the inter-ring C9—C12 bond [1.494 (3) Å] suggests that it is essentially a single bond. A somewhat surprising feature is that the bulky C11 methyl group lies close to atom O4 rather than, as might be expected, close to the much smaller H atom attached to atom C13. As a result, atom O4 is significantly displaced [by 0.387 (3) Å] from the least-squares plane of its naphthoquinonyl unit (C12–C22/O5/O6). Conversely, atom C11 shows no significant deviation [displacement = 0.018 (2) Å] from the C1–C11/O1–O3 least-squares plane.

Both OH groups participate in bifurcated intra/inter-molecular hydrogen bonds to C=O acceptors (Table 2). The intramolecular O—H···O bonds are much shorter and

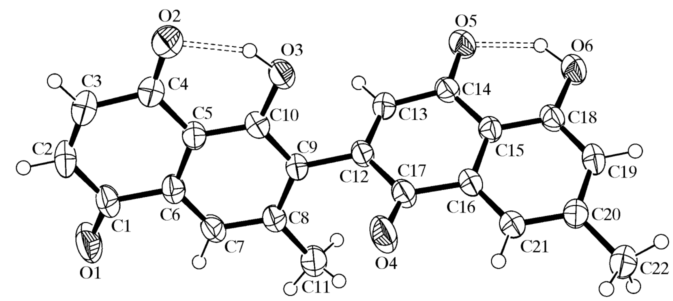



**Figure 1**
The asymmetric unit of (I) (50% probability displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are indicated by dashed lines.

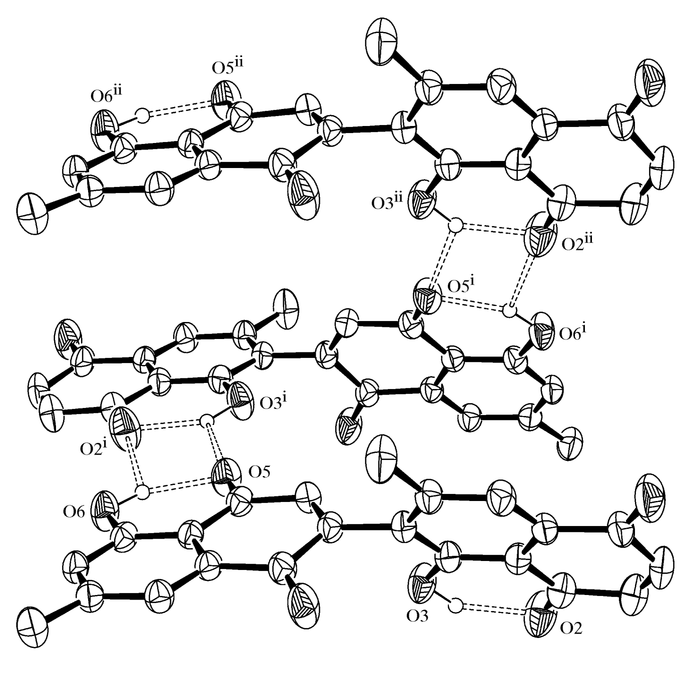



**Figure 2**
A detail of (I), showing the [010] stacking resulting from O—H···O hydrogen bonds (50% probability displacement ellipsoids). [Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ix) $x, 1 + y, z$.]

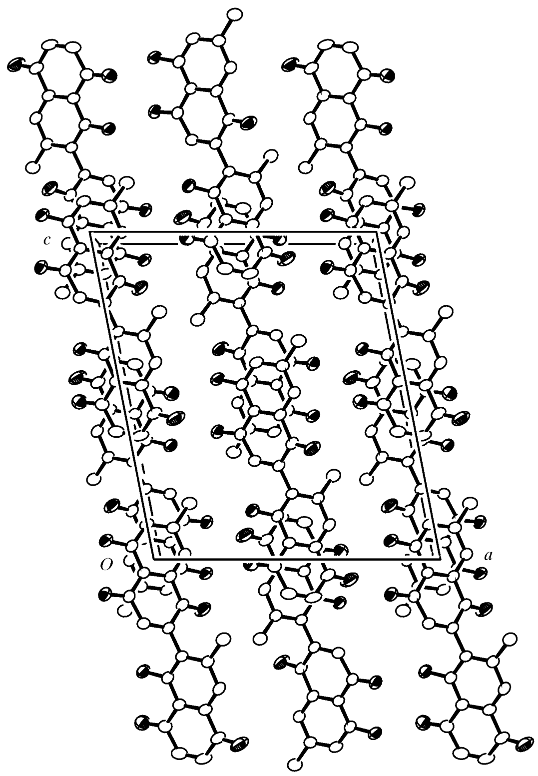



**Figure 3**
The crystal packing of (I), projected on to (010) (H atoms have been omitted for clarity).

stronger than the intermolecular links. This difference results in an 'unbalanced' hydrogen-bonding network, in which atoms O2 and O5 accept two hydrogen bonds each (one intramolecular and one intermolecular), and atoms O1 and O4 do not accept any conventional hydrogen bonds. Together (Fig. 2), the O—H···O bonds generate infinite [010] stacks of molecules of (I), generated by a $2_1$ screw axis. A *PLATON* (Spek, 2003) analysis of (I) indicated the possible presence of two short C—H···O interactions arising from methyl group H atoms (Table 2), although such interactions are expected to be very weak for such 'unactivated' bonds (Desiraju & Steiner, 1999). Interestingly, the acceptor atoms are the 'underbonded' atoms O1 and O4 (see above). If they are not merely packing artefacts, these C—H···O interactions may provide some coherence between adjacent [010] stacks of molecules in the *a* direction. Possible $\pi$–$\pi$ stacking interactions, with a centroid–centroid separation of less than 4.0 Å, are listed in Table 3. The relatively large value of $\Delta$ in each case suggests that these interactions are weak.

The structure shown in Fig. 1 is dissymmetric, but crystal symmetry generates a racemic mixture that is consistent with the lack of optical activity shown by (I) in solution (Lillie *et al.*, 1976). The interconversion of the two enantiomeric forms would be expected to occur readily in solution by analogy with the behaviour of trisubstituted biphenyls such as (II) (Adams & Teeter, 1940), which undergo rapid racemization in solution. The crystal packing of (I) is shown in Fig. 3.

## Experimental

Diospyrin was isolated from *Diospyros montana* (*cf.* Lillie *et al.*, 1976) and recrystallized from chloroform as an intense orange powder accompanied by one or two well faceted orange plates.

*Crystal data*

$C_{22}H_{14}O_6$
$M_r$ = 374.33
Monoclinic, $P2_1/n$
$a$ = 13.5603 (10) Å
$b$ = 7.8549 (6) Å
$c$ = 15.8121 (11) Å
$\beta$ = 101.063 (2)°
$V$ = 1652.9 (2) Å$^3$
$Z$ = 4
$D_x$ = 1.504 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2069 reflections
$\theta$ = 2.6–25.5°
$\mu$ = 0.11 mm$^{-1}$
$T$ = 293 (2) K
Plate, orange
0.36 × 0.29 × 0.05 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min}$ = 0.920, $T_{max}$ = 0.995
10 116 measured reflections
3091 independent reflections
1739 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.039
$\theta_{max}$ = 25.6°
$h = -16 \rightarrow 14$
$k = -9 \rightarrow 8$
$l = -19 \rightarrow 19$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.127
$S$ = 0.92
3091 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

**Table 1**
Selected interatomic distances (Å).

| | | | |
|---|---|---|---|
| O1—C1 | 1.214 (3) | C8—C11 | 1.499 (3) |
| O2—C4 | 1.232 (3) | C9—C10 | 1.404 (3) |
| O3—C10 | 1.341 (2) | C9—C12 | 1.494 (3) |
| O4—C17 | 1.218 (2) | C12—C13 | 1.337 (3) |
| O5—C14 | 1.233 (2) | C12—C17 | 1.485 (3) |
| O6—C18 | 1.340 (2) | C13—C14 | 1.468 (3) |
| C1—C2 | 1.471 (3) | C14—C15 | 1.454 (3) |
| C1—C6 | 1.483 (3) | C15—C18 | 1.402 (3) |
| C2—C3 | 1.320 (3) | C15—C16 | 1.408 (3) |
| C3—C4 | 1.480 (3) | C16—C21 | 1.378 (3) |
| C4—C5 | 1.452 (3) | C16—C17 | 1.487 (3) |
| C5—C10 | 1.407 (3) | C18—C19 | 1.381 (3) |
| C5—C6 | 1.409 (3) | C19—C20 | 1.379 (3) |
| C6—C7 | 1.370 (3) | C20—C21 | 1.396 (3) |
| C7—C8 | 1.397 (3) | C20—C22 | 1.504 (3) |
| C8—C9 | 1.391 (3) | | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H1···O2 | 0.96 | 1.77 | 2.607 (2) | 144 |
| O3—H1···O5$^{i}$ | 0.96 | 2.40 | 2.986 (2) | 119 |
| O6—H2···O5 | 0.99 | 1.78 | 2.630 (2) | 142 |
| O6—H2···O2$^{ii}$ | 0.99 | 2.36 | 2.980 (2) | 120 |
| C11—H6···O4$^{iii}$ | 0.96 | 2.38 | 3.331 (3) | 170 |
| C22—H12···O1$^{iv}$ | 0.96 | 2.52 | 3.415 (3) | 156 |

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

**Table 3**
$\pi$–$\pi$ stacking interactions in (I).

*Cg*1 is the centroid of the C1–C6 ring, *Cg*2 is the centroid of the C5–C10 ring, *Cg*3 is the centroid of the C12–C17 ring and *Cg*4 is the centroid of the C15/C16/C18–C21 ring. $\varphi$ is the dihedral angle (°) between the planes of the rings, $d$ is the distance (Å) between the ring centroids and $\Delta$ is the displacement (Å) of the centroid of ring 2 relative to the intersection point of the normal to the centroid of ring 1 and the least-squares plane of ring 2.

| Ring 1 | Ring 2 | $\varphi$ | $d$ | $\Delta$ |
|---|---|---|---|---|
| *Cg*1 | $Cg2^{v}$ | 0.0 | 3.9219 (14) | 2.15 |
| *Cg*1 | $Cg2^{vi}$ | 2.9 | 3.7161 (14) | 1.17 |
| *Cg*3 | $Cg4^{vii}$ | 4.5 | 3.9486 (14) | 2.02 |
| *Cg*4 | $Cg4^{viii}$ | 0.0 | 3.6772 (14) | 1.36 |

Symmetry codes: (v) $1-x, -y, -z$; (vi) $1-x, 1-y, -z$; (vii) $1-x, 1-y, 1-z$; (viii) $1-x, -y, 1-z$.

H atoms bonded to O atoms were found in difference maps and refined as riding. H atoms bonded to C atoms were placed in calculated positions (C—H = 0.96–0.98 Å) and refined as riding, allowing for free rotation of the rigid methyl groups. $U_{iso}$(H) values were constrained to be $1.2U_{eq}$(attached atom) [$1.5U_{eq}$(C) for methyl H atoms].

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1005). Services for accessing these data are described at the back of the journal.

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supporting information

*Acta Cryst.* (2004). C**60**, o399–o401 [doi:10.1107/S0108270104007826]

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### 1′,5-dihydroxy-3′,7-dimethyl-2,2′-binaphthalene-1,4,5′,8′-tetrone

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$h$ = −16→14
$k$ = −9→8
$l$ = −19→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.127
$S$ = 0.92
3091 reflections
255 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difmap (O-H) and geom (C-H)
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.67119 (14) | 0.3929 (3) | −0.06871 (11) | 0.0706 (6) |
| O2 | 0.33522 (12) | 0.0988 (3) | −0.01421 (10) | 0.0661 (6) |
| O3 | 0.37668 (11) | 0.1809 (2) | 0.14853 (9) | 0.0505 (5) |
| H1 | 0.3427 | 0.1212 | 0.0983 | 0.061* |
| O4 | 0.62949 (13) | 0.1313 (2) | 0.33927 (10) | 0.0634 (5) |
| O5 | 0.30530 (11) | 0.4599 (2) | 0.39318 (9) | 0.0496 (5) |
| O6 | 0.34246 (11) | 0.3695 (2) | 0.55636 (9) | 0.0510 (5) |
| H2 | 0.3024 | 0.4207 | 0.5036 | 0.061* |
| C1 | 0.59863 (18) | 0.3184 (3) | −0.05253 (14) | 0.0449 (6) |
| C2 | 0.53119 (19) | 0.2234 (3) | −0.12023 (15) | 0.0563 (7) |
| H3 | 0.5485 | 0.2126 | −0.1741 | 0.068* |
| C3 | 0.44699 (19) | 0.1528 (3) | −0.10728 (15) | 0.0560 (7) |
| H4 | 0.4064 | 0.0953 | −0.1524 | 0.067* |
| C4 | 0.41564 (17) | 0.1630 (3) | −0.02276 (14) | 0.0449 (6) |
| C5 | 0.48317 (15) | 0.2454 (3) | 0.04771 (12) | 0.0369 (5) |
| C6 | 0.57353 (16) | 0.3201 (3) | 0.03472 (13) | 0.0373 (5) |
| C7 | 0.63802 (15) | 0.3939 (3) | 0.10202 (13) | 0.0416 (6) |
| H5 | 0.6974 | 0.4424 | 0.0923 | 0.050* |
| C8 | 0.61665 (15) | 0.3981 (3) | 0.18499 (13) | 0.0388 (5) |
| C9 | 0.52763 (15) | 0.3260 (3) | 0.19949 (13) | 0.0346 (5) |
| C10 | 0.46086 (15) | 0.2503 (3) | 0.13101 (13) | 0.0364 (5) |
| C11 | 0.68818 (17) | 0.4857 (4) | 0.25561 (14) | 0.0591 (8) |
| H6 | 0.7400 | 0.5406 | 0.2319 | 0.089* |
| H7 | 0.7178 | 0.4034 | 0.2978 | 0.089* |
| H8 | 0.6525 | 0.5692 | 0.2824 | 0.089* |
| C12 | 0.50020 (14) | 0.3249 (3) | 0.28660 (13) | 0.0346 (5) |
| C13 | 0.41787 (15) | 0.4030 (3) | 0.30217 (13) | 0.0367 (5) |
| H9 | 0.3792 | 0.4660 | 0.2581 | 0.044* |
| C14 | 0.38558 (15) | 0.3939 (3) | 0.38549 (13) | 0.0353 (5) |
| C15 | 0.45032 (14) | 0.3069 (3) | 0.45627 (12) | 0.0326 (5) |
| C16 | 0.53997 (14) | 0.2289 (3) | 0.44382 (13) | 0.0345 (5) |
| C17 | 0.56283 (15) | 0.2224 (3) | 0.35557 (13) | 0.0383 (5) |
| C18 | 0.42673 (15) | 0.3008 (3) | 0.53877 (13) | 0.0358 (5) |
| C19 | 0.49258 (15) | 0.2243 (3) | 0.60535 (14) | 0.0395 (5) |
| H10 | 0.4759 | 0.2204 | 0.6597 | 0.047* |

| | | | | |
|---|---|---|---|---|
| C20 | 0.58219 (15) | 0.1535 (3) | 0.59406 (13) | 0.0374 (5) |
| C21 | 0.60467 (15) | 0.1542 (3) | 0.51152 (13) | 0.0378 (5) |
| H11 | 0.6637 | 0.1039 | 0.5022 | 0.045* |
| C22 | 0.65535 (16) | 0.0810 (3) | 0.66902 (13) | 0.0513 (6) |
| H12 | 0.6970 | −0.0022 | 0.6485 | 0.077* |
| H13 | 0.6191 | 0.0281 | 0.7085 | 0.077* |
| H14 | 0.6967 | 0.1707 | 0.6979 | 0.077* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0842 (13) | 0.0900 (15) | 0.0464 (11) | −0.0220 (11) | 0.0350 (10) | −0.0037 (10) |
| O2 | 0.0535 (11) | 0.0962 (16) | 0.0487 (11) | −0.0201 (10) | 0.0100 (8) | −0.0171 (10) |
| O3 | 0.0442 (9) | 0.0720 (13) | 0.0388 (9) | −0.0181 (8) | 0.0166 (7) | −0.0120 (8) |
| O4 | 0.0697 (11) | 0.0819 (14) | 0.0463 (10) | 0.0361 (10) | 0.0307 (9) | 0.0157 (9) |
| O5 | 0.0422 (9) | 0.0669 (12) | 0.0430 (9) | 0.0149 (8) | 0.0162 (7) | 0.0027 (8) |
| O6 | 0.0476 (9) | 0.0729 (13) | 0.0364 (9) | 0.0147 (8) | 0.0178 (7) | 0.0019 (8) |
| C1 | 0.0545 (15) | 0.0507 (16) | 0.0342 (13) | 0.0013 (11) | 0.0200 (11) | 0.0055 (11) |
| C2 | 0.0701 (17) | 0.075 (2) | 0.0270 (12) | 0.0019 (14) | 0.0172 (12) | −0.0051 (12) |
| C3 | 0.0610 (17) | 0.074 (2) | 0.0311 (13) | −0.0001 (13) | 0.0051 (12) | −0.0075 (12) |
| C4 | 0.0448 (14) | 0.0547 (17) | 0.0346 (13) | 0.0006 (11) | 0.0064 (11) | −0.0037 (11) |
| C5 | 0.0406 (12) | 0.0417 (15) | 0.0293 (12) | 0.0011 (10) | 0.0091 (10) | −0.0004 (10) |
| C6 | 0.0446 (13) | 0.0395 (14) | 0.0295 (12) | 0.0031 (10) | 0.0118 (10) | 0.0033 (10) |
| C7 | 0.0395 (13) | 0.0507 (16) | 0.0382 (13) | −0.0068 (10) | 0.0169 (10) | −0.0001 (11) |
| C8 | 0.0383 (12) | 0.0472 (15) | 0.0325 (12) | −0.0038 (10) | 0.0111 (10) | 0.0002 (10) |
| C9 | 0.0369 (12) | 0.0413 (15) | 0.0271 (11) | 0.0010 (9) | 0.0095 (9) | 0.0013 (9) |
| C10 | 0.0359 (12) | 0.0417 (15) | 0.0336 (12) | 0.0001 (9) | 0.0119 (9) | 0.0005 (10) |
| C11 | 0.0502 (15) | 0.090 (2) | 0.0382 (13) | −0.0199 (13) | 0.0119 (11) | −0.0076 (14) |
| C12 | 0.0362 (12) | 0.0401 (14) | 0.0298 (11) | −0.0040 (9) | 0.0122 (9) | −0.0014 (10) |
| C13 | 0.0392 (12) | 0.0421 (14) | 0.0291 (11) | 0.0011 (10) | 0.0075 (9) | 0.0029 (10) |
| C14 | 0.0339 (12) | 0.0397 (14) | 0.0340 (12) | −0.0016 (10) | 0.0104 (9) | −0.0035 (10) |
| C15 | 0.0353 (12) | 0.0349 (13) | 0.0289 (11) | −0.0008 (9) | 0.0092 (9) | −0.0026 (9) |
| C16 | 0.0373 (12) | 0.0363 (14) | 0.0325 (12) | −0.0021 (9) | 0.0137 (9) | −0.0018 (10) |
| C17 | 0.0403 (12) | 0.0429 (14) | 0.0353 (12) | 0.0043 (10) | 0.0161 (10) | 0.0019 (10) |
| C18 | 0.0366 (12) | 0.0399 (14) | 0.0336 (12) | −0.0013 (9) | 0.0132 (10) | −0.0050 (10) |
| C19 | 0.0488 (14) | 0.0436 (15) | 0.0291 (11) | −0.0026 (11) | 0.0148 (10) | −0.0014 (10) |
| C20 | 0.0419 (13) | 0.0400 (14) | 0.0306 (12) | −0.0035 (9) | 0.0077 (10) | 0.0004 (10) |
| C21 | 0.0363 (12) | 0.0443 (15) | 0.0344 (12) | 0.0029 (9) | 0.0107 (10) | 0.0010 (10) |
| C22 | 0.0545 (15) | 0.0632 (18) | 0.0362 (13) | 0.0066 (12) | 0.0087 (11) | 0.0075 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.214 (3) | C9—C12 | 1.494 (3) |
| O2—C4 | 1.232 (3) | C11—H6 | 0.9600 |
| O3—C10 | 1.341 (2) | C11—H7 | 0.9600 |
| O3—H1 | 0.9612 | C11—H8 | 0.9600 |
| O4—C17 | 1.218 (2) | C12—C13 | 1.337 (3) |
| O5—C14 | 1.233 (2) | C12—C17 | 1.485 (3) |

| | | | |
|---|---|---|---|
| O6—C18 | 1.340 (2) | C13—C14 | 1.468 (3) |
| O6—H2 | 0.9899 | C13—H9 | 0.9300 |
| C1—C2 | 1.471 (3) | C14—C15 | 1.454 (3) |
| C1—C6 | 1.483 (3) | C15—C18 | 1.402 (3) |
| C2—C3 | 1.320 (3) | C15—C16 | 1.408 (3) |
| C2—H3 | 0.9300 | C16—C21 | 1.378 (3) |
| C3—C4 | 1.480 (3) | C16—C17 | 1.487 (3) |
| C3—H4 | 0.9300 | C18—C19 | 1.381 (3) |
| C4—C5 | 1.452 (3) | C19—C20 | 1.379 (3) |
| C5—C10 | 1.407 (3) | C19—H10 | 0.9300 |
| C5—C6 | 1.409 (3) | C20—C21 | 1.396 (3) |
| C6—C7 | 1.370 (3) | C20—C22 | 1.504 (3) |
| C7—C8 | 1.397 (3) | C21—H11 | 0.9300 |
| C7—H5 | 0.9300 | C22—H12 | 0.9600 |
| C8—C9 | 1.391 (3) | C22—H13 | 0.9600 |
| C8—C11 | 1.499 (3) | C22—H14 | 0.9600 |
| C9—C10 | 1.404 (3) | | |

| | | | |
|---|---|---|---|
| C10—O3—H1 | 108.7 | H7—C11—H8 | 109.5 |
| C18—O6—H2 | 109.9 | C13—C12—C17 | 119.58 (18) |
| O1—C1—C2 | 120.5 (2) | C13—C12—C9 | 122.10 (19) |
| O1—C1—C6 | 122.1 (2) | C17—C12—C9 | 118.15 (17) |
| C2—C1—C6 | 117.4 (2) | C12—C13—C14 | 123.1 (2) |
| C3—C2—C1 | 122.4 (2) | C12—C13—H9 | 118.4 |
| C3—C2—H3 | 118.8 | C14—C13—H9 | 118.4 |
| C1—C2—H3 | 118.8 | O5—C14—C15 | 122.43 (19) |
| C2—C3—C4 | 121.6 (2) | O5—C14—C13 | 119.29 (19) |
| C2—C3—H4 | 119.2 | C15—C14—C13 | 118.28 (18) |
| C4—C3—H4 | 119.2 | C18—C15—C16 | 118.19 (19) |
| O2—C4—C5 | 122.6 (2) | C18—C15—C14 | 121.35 (18) |
| O2—C4—C3 | 119.4 (2) | C16—C15—C14 | 120.44 (18) |
| C5—C4—C3 | 118.0 (2) | C21—C16—C15 | 120.96 (19) |
| C10—C5—C6 | 118.31 (19) | C21—C16—C17 | 119.85 (18) |
| C10—C5—C4 | 120.88 (19) | C15—C16—C17 | 119.16 (19) |
| C6—C5—C4 | 120.80 (19) | O4—C17—C12 | 120.42 (19) |
| C7—C6—C5 | 120.44 (19) | O4—C17—C16 | 121.0 (2) |
| C7—C6—C1 | 120.0 (2) | C12—C17—C16 | 118.52 (18) |
| C5—C6—C1 | 119.5 (2) | O6—C18—C19 | 117.99 (18) |
| C6—C7—C8 | 121.53 (19) | O6—C18—C15 | 122.37 (19) |
| C6—C7—H5 | 119.2 | C19—C18—C15 | 119.63 (18) |
| C8—C7—H5 | 119.2 | C20—C19—C18 | 122.28 (19) |
| C9—C8—C7 | 119.21 (19) | C20—C19—H10 | 118.9 |
| C9—C8—C11 | 121.46 (19) | C18—C19—H10 | 118.9 |
| C7—C8—C11 | 119.29 (19) | C19—C20—C21 | 118.39 (19) |
| C8—C9—C10 | 119.79 (18) | C19—C20—C22 | 121.02 (19) |
| C8—C9—C12 | 122.12 (19) | C21—C20—C22 | 120.58 (19) |
| C10—C9—C12 | 118.09 (17) | C16—C21—C20 | 120.47 (19) |
| O3—C10—C9 | 117.48 (18) | C16—C21—H11 | 119.8 |

| | | | |
|---|---|---|---|
| O3—C10—C5 | 121.79 (18) | C20—C21—H11 | 119.8 |
| C9—C10—C5 | 120.72 (18) | C20—C22—H12 | 109.5 |
| C8—C11—H6 | 109.5 | C20—C22—H13 | 109.5 |
| C8—C11—H7 | 109.5 | H12—C22—H13 | 109.5 |
| H6—C11—H7 | 109.5 | C20—C22—H14 | 109.5 |
| C8—C11—H8 | 109.5 | H12—C22—H14 | 109.5 |
| H6—C11—H8 | 109.5 | H13—C22—H14 | 109.5 |

| | | | |
|---|---|---|---|
| C8—C9—C12—C17 | −66.2 (3) | C10—C9—C12—C17 | 113.3 (2) |
| C8—C9—C12—C13 | 118.5 (2) | C10—C9—C12—C13 | −61.9 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H1···O2 | 0.96 | 1.77 | 2.607 (2) | 144 |
| O3—H1···O5$^{i}$ | 0.96 | 2.40 | 2.986 (2) | 119 |
| O6—H2···O5 | 0.99 | 1.78 | 2.630 (2) | 142 |
| O6—H2···O2$^{ii}$ | 0.99 | 2.36 | 2.980 (2) | 120 |
| C11—H6···O4$^{iii}$ | 0.96 | 2.38 | 3.331 (3) | 170 |
| C22—H12···O1$^{iv}$ | 0.96 | 2.52 | 3.415 (3) | 156 |

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