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## Structure Reports

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# 9-(4-Hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6-tetrahydro-9H-xanthene-1,8(2H,7H)-dione

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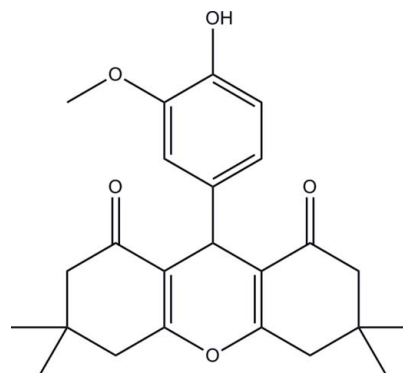
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.136; data-to-parameter ratio = 22.0.

In the title compound,  $\text{C}_{24}\text{H}_{28}\text{O}_5$ , the two cyclohexene rings adopt envelope conformations, and the planes through the coplanar atoms makes dihedral angles of 82.86 (6) and 77.90 (6)° with the benzene ring. The two cyclohexene rings make a dihedral angle of 5.33 (6)° between their least-squares planes. The pyran ring adopts a flattened boat conformation. In the crystal packing, molecules are linked into two-dimensional networks parallel to the  $ab$  plane via  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  interactions.

## Related literature

For the synthesis of the title compound, see: Venkatesan *et al.* (2008). For general background to and the biological activity of xanthene derivatives, see: Hafez *et al.* (2008); Ashry *et al.* (2006); Sill & Sweet (1977); Ion (1997); Chibale *et al.* (2003). For reference bond lengths, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986). For ring conformations, see: Cremer & Pople (1975).



## Experimental

### Crystal data

|  |                                   |
|--|-----------------------------------|
| $\text{C}_{24}\text{H}_{28}\text{O}_5$ | $V = 4100.6$ (6) Å <sup>3</sup>   |
| $M_r = 396.46$                         | $Z = 8$                           |
| Orthorhombic, $Pbca$                   | Mo $K\alpha$ radiation            |
| $a = 11.4861$ (10) Å                   | $\mu = 0.09$ mm <sup>-1</sup>     |
| $b = 11.8659$ (11) Å                   | $T = 100$ K                       |
| $c = 30.087$ (3) Å                     | $0.35 \times 0.30 \times 0.24$ mm |

### Data collection

|  |  |
|--|--|
| Bruker APEXII DUO area-detector diffractometer           | 26584 measured reflections             |
| Absorption correction: multi-scan (SADABS; Bruker, 2009) | 5972 independent reflections           |
| $T_{\min} = 0.970$ , $T_{\max} = 0.979$                  | 4634 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.046$               |

### Refinement

|                                 |  |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.136$               | $\Delta\rho_{\max} = 0.57$ e Å <sup>-3</sup>                           |
| $S = 1.06$                      | $\Delta\rho_{\min} = -0.38$ e Å <sup>-3</sup>                          |
| 5972 reflections                |  |
| 271 parameters                  |  |

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                                 | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O5}-\text{H14O}\cdots\text{O3}^{\text{i}}$    | 0.86 (2)     | 1.95 (2)           | 2.7319 (13) | 151 (2)              |
| $\text{C2}-\text{H2A}\cdots\text{O2}^{\text{ii}}$    | 0.97         | 2.55               | 3.5003 (16) | 165                  |
| $\text{C20}-\text{H20C}\cdots\text{O2}^{\text{iii}}$ | 0.96         | 2.58               | 3.4646 (17) | 154                  |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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§ Thomson Reuters ResearcherID: A-5525-2009.

¶ Thomson Reuters ResearcherID: A-3561-2009.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2454).

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## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Ashry, E. S. H. E., Awad, L. F., Ibrahim, E. S. I. & Bdeewy, O. K. (2006). *Arkivoc*, **2**, 178–186.
- Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chibale, K., Visser, M., Schalkwyk, D., Smith, P. J., Saravanamuthu, A. & Fairlamb, A. H. (2003). *Tetrahedron*, **59**, 2289–2296.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Hafez, H. N., Hegab, M. I., Ahmed-Farag, I. S. & El-Gazzar, A. B. A. (2008). *Bioorg. Med. Chem. Lett.* **18**, 4538–4543.
- Ion, R. M. (1997). *Prog. Catal.* **2**, 55–76.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sill, A. D. & Sweet, F. W. (1977). US Patent No. 4008240.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Venkatesan, K., Pujari, S. S., Lahoti, R. J. & Srinivasan, K. V. (2008). *Ultrason. Sonochem.* **15**, 548–553.

## supporting information

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## 9-(4-Hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6-tetrahydro-9H-xanthene-1,8(2H,7H)-dione

Noorhafizah Hasanudin, Aisyah Saad Abdul Rahim, Nornisah Mohamed, Ching Kheng Quah and Hoong-Kun Fun

### S1. Comment

Xanthene derivatives especially benzoxanthenes are well-known in organic synthesis due to their biologically active properties such as anti-inflammatory (Hafez *et al.*, 2008), antimicrobial (Ashry *et al.*, 2006), antiviral (Sill & Sweet, 1977) activities and as well as being used in photodynamic therapy (Ion, 1997). Molecules based on the 9,9-dimethylxanthene moiety have inhibitory activity towards trypanothione reductase (TryR) (Chibale *et al.*, 2003). In view of its importance in this field, the crystal structure of the title compound was determined and the results are presented here.

The bond lengths (Allen *et al.*, 1987) and angles in the title compound (Fig. 1) are within normal ranges. The two cyclohexene rings, C1—C6 and C8—C13, adopt an envelope conformation, and the plane through the coplanar atoms makes dihedral angles of 82.86 (6)° and 77.90 (6)°, respectively, with the benzene ring (C14—C19). The puckering parameters (Cremer & Pople, 1975) are  $Q = 0.4872$  (14) Å,  $\Theta = 125.01$  (16)° and  $\varphi = 307.7$  (2)° for the C1—C6 ring,  $Q = 0.4698$  (14) Å,  $\Theta = 56.48$  (17)° and  $\varphi = 172.6$  (2)° for the C8—C13 ring. The two cyclohexene rings make a dihedral angle of 5.33 (6)° between their least-squares planes. The pyran ring (O1/C1/C6—C8/C13) adopts a flattened boat conformation with atoms C7 and O1 deviating by 0.150 (1) and 0.111 (1) Å, respectively, from the base of the boat.

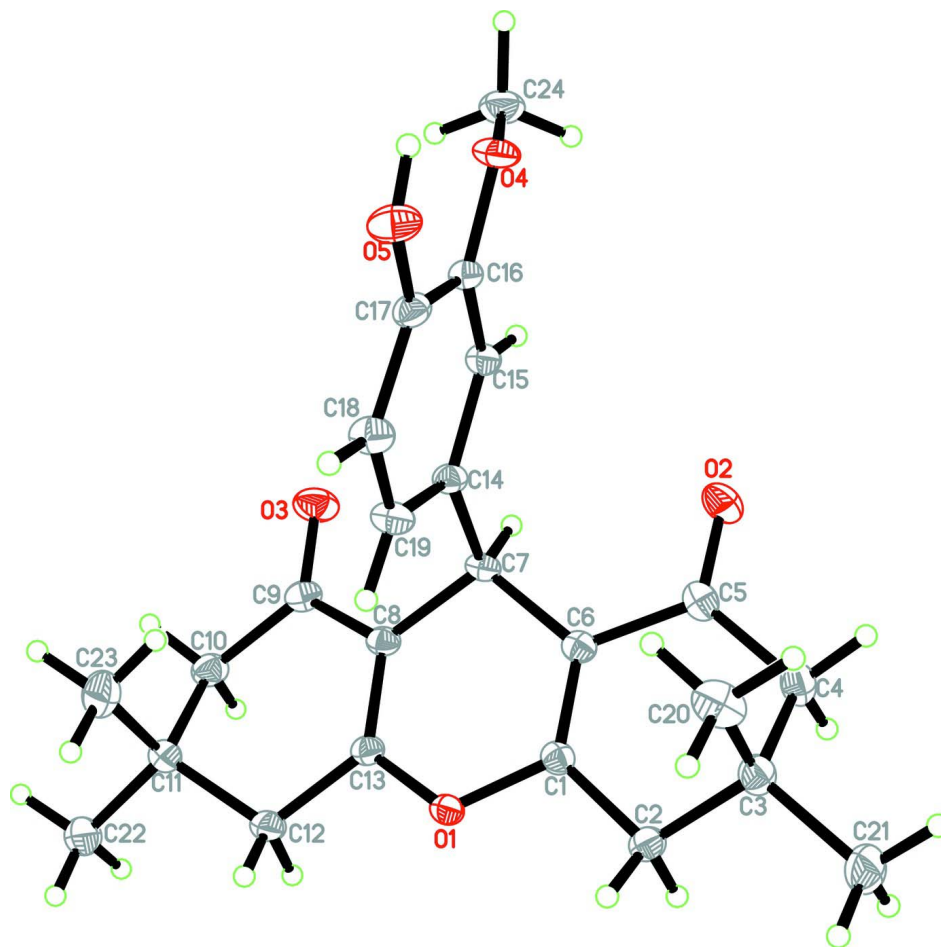
In the crystal packing (Fig. 2), the molecules are linked into two-dimensional networks parallel to the *ab* plane via O5—H14O⋯O3, C2—H2A⋯O2 and C20—H20C⋯O2 interactions (Table 1).

### S2. Experimental

The synthesis of the title compound was performed according to the procedure described in the literature (Venkatesan *et al.*, 2008). A mixture of vanilin (90 mg, 0.59 mmol), dimedone (160 mg, 1.14 mmol), *p*-toluenesulfonic acid (2 mg) in MeOH (4 ml) and water (2 ml) was heated to 50 °C in N<sub>2</sub> atmosphere for about 20 min. Good quality crystals suitable for characterisation by X-ray crystallography were obtained by recrystallisation from hot methanol.

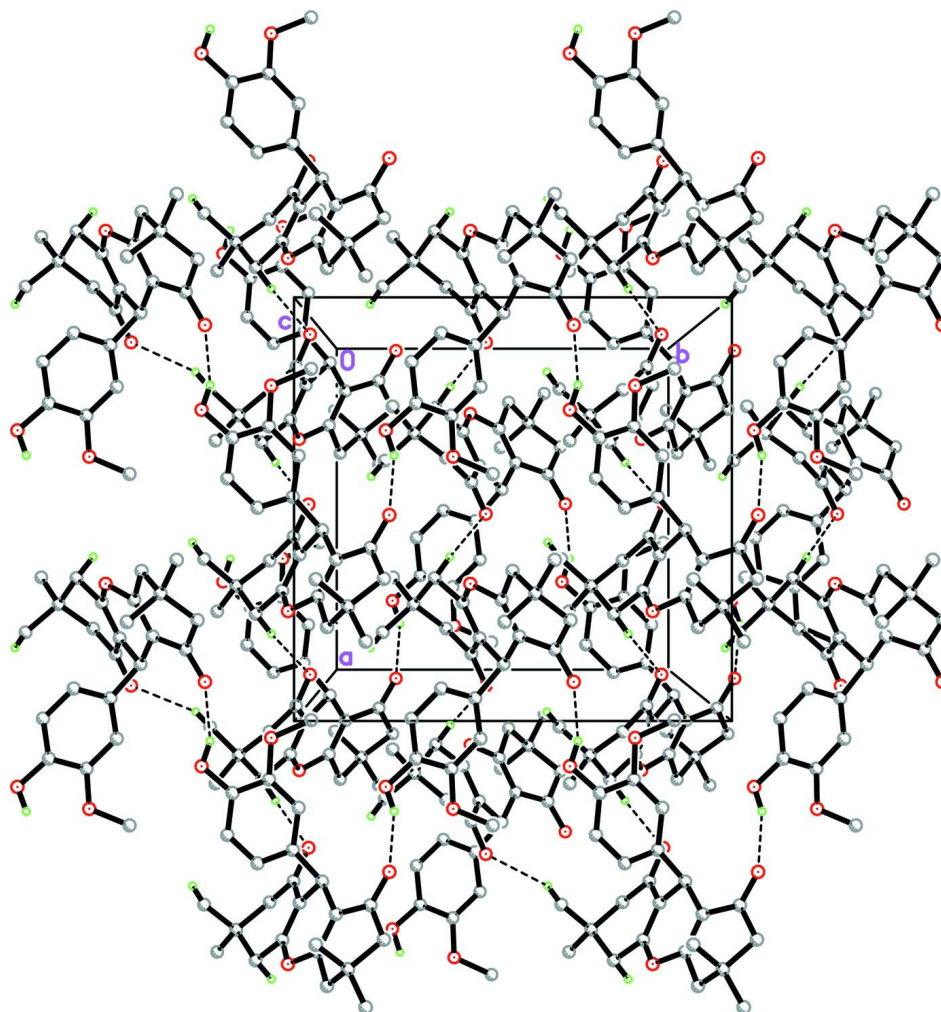
### S3. Refinement

Atom H14O was located in a difference Fourier map and allowed to refine freely. All other hydrogen atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5 U_{\text{eq}}(\text{C})$ . A rotating-group model was applied for the methyl groups.



**Figure 1**

The molecular structure of the title compound, showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

**Figure 2**

The crystal structure of the title compound viewed along the *c* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

**9-(4-Hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6-tetrahydro- 9*H*-xanthene-1,8(2*H*,7*H*)-dione**

*Crystal data*

$C_{24}H_{28}O_5$

$M_r = 396.46$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 11.4861$  (10) Å

$b = 11.8659$  (11) Å

$c = 30.087$  (3) Å

$V = 4100.6$  (6) Å<sup>3</sup>

$Z = 8$

$F(000) = 1696$

$D_x = 1.284$  Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5544 reflections

$\theta = 2.2$ – $31.4^\circ$

$\mu = 0.09$  mm<sup>-1</sup>

$T = 100$  K

Block, colourless

$0.35 \times 0.30 \times 0.24$  mm

*Data collection*

Bruker APEXII DUO CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.970$ ,  $T_{\max} = 0.979$

26584 measured reflections

5972 independent reflections

4634 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 30.0^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -16 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -20 \rightarrow 42$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.136$

$S = 1.06$

5972 reflections

271 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.8139P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

*Special details*

**Experimental.** The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**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.

**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 ( $\text{\AA}^2$ )*

|     | <i>x</i>      | <i>y</i>     | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|-------------|----------------------------------|
| O1  | -0.28861 (7)  | 0.40281 (8)  | 0.37337 (3) | 0.01617 (19)                     |
| O2  | 0.01386 (8)   | 0.44676 (8)  | 0.26832 (3) | 0.0228 (2)                       |
| O3  | -0.01627 (8)  | 0.68315 (9)  | 0.41472 (4) | 0.0257 (2)                       |
| O4  | 0.35090 (8)   | 0.35573 (8)  | 0.36534 (3) | 0.0207 (2)                       |
| O5  | 0.27890 (8)   | 0.17322 (8)  | 0.41056 (4) | 0.0225 (2)                       |
| C1  | -0.23302 (10) | 0.38185 (10) | 0.33355 (4) | 0.0146 (2)                       |
| C2  | -0.30172 (10) | 0.30335 (11) | 0.30502 (4) | 0.0170 (2)                       |
| H2A | -0.3616       | 0.3454       | 0.2895      | 0.020*                           |
| H2B | -0.3398       | 0.2477       | 0.3236      | 0.020*                           |
| C3  | -0.22358 (11) | 0.24318 (11) | 0.27099 (4) | 0.0190 (3)                       |
| C4  | -0.15068 (12) | 0.33410 (12) | 0.24770 (5) | 0.0215 (3)                       |
| H4A | -0.0983       | 0.2979       | 0.2268      | 0.026*                           |
| H4B | -0.2023       | 0.3826       | 0.2308      | 0.026*                           |
| C5  | -0.08000 (11) | 0.40592 (10) | 0.27917 (4) | 0.0171 (2)                       |

|      |               |              |             |            |
|------|---------------|--------------|-------------|------------|
| C6   | -0.12984 (10) | 0.42841 (10) | 0.32340 (4) | 0.0142 (2) |
| C7   | -0.05937 (10) | 0.49443 (10) | 0.35702 (4) | 0.0142 (2) |
| H7A  | -0.0228       | 0.5590       | 0.3423      | 0.017*     |
| C8   | -0.14118 (10) | 0.53630 (10) | 0.39271 (4) | 0.0143 (2) |
| C9   | -0.10776 (11) | 0.63245 (11) | 0.42079 (4) | 0.0172 (2) |
| C10  | -0.19236 (11) | 0.67093 (11) | 0.45628 (5) | 0.0195 (3) |
| H10A | -0.2428       | 0.7283       | 0.4438      | 0.023*     |
| H10B | -0.1487       | 0.7054       | 0.4803      | 0.023*     |
| C11  | -0.26798 (11) | 0.57635 (11) | 0.47544 (4) | 0.0185 (3) |
| C12  | -0.32808 (11) | 0.51647 (11) | 0.43638 (4) | 0.0182 (3) |
| H12A | -0.3646       | 0.4479       | 0.4471      | 0.022*     |
| H12B | -0.3888       | 0.5649       | 0.4247      | 0.022*     |
| C13  | -0.24524 (10) | 0.48756 (10) | 0.39991 (4) | 0.0145 (2) |
| C14  | 0.03504 (10)  | 0.41644 (10) | 0.37528 (4) | 0.0144 (2) |
| C15  | 0.15186 (10)  | 0.43068 (10) | 0.36324 (4) | 0.0150 (2) |
| H15A | 0.1742        | 0.4937       | 0.3470      | 0.018*     |
| C16  | 0.23459 (10)  | 0.35118 (11) | 0.37548 (4) | 0.0154 (2) |
| C17  | 0.20159 (11)  | 0.25532 (10) | 0.39955 (4) | 0.0163 (2) |
| C18  | 0.08671 (11)  | 0.24362 (11) | 0.41294 (5) | 0.0192 (3) |
| H18A | 0.0648        | 0.1820       | 0.4301      | 0.023*     |
| C19  | 0.00419 (11)  | 0.32338 (11) | 0.40088 (5) | 0.0186 (3) |
| H19A | -0.0726       | 0.3146       | 0.4100      | 0.022*     |
| C20  | -0.14395 (12) | 0.15751 (11) | 0.29401 (5) | 0.0253 (3) |
| H20A | -0.1906       | 0.1025       | 0.3092      | 0.038*     |
| H20B | -0.0951       | 0.1957       | 0.3151      | 0.038*     |
| H20C | -0.0963       | 0.1207       | 0.2722      | 0.038*     |
| C21  | -0.29993 (13) | 0.18345 (13) | 0.23661 (5) | 0.0291 (3) |
| H21A | -0.3498       | 0.1304       | 0.2514      | 0.044*     |
| H21B | -0.2513       | 0.1444       | 0.2157      | 0.044*     |
| H21C | -0.3465       | 0.2381       | 0.2212      | 0.044*     |
| C22  | -0.36133 (12) | 0.62585 (14) | 0.50611 (5) | 0.0282 (3) |
| H22A | -0.3246       | 0.6625       | 0.5308      | 0.042*     |
| H22B | -0.4107       | 0.5664       | 0.5168      | 0.042*     |
| H22C | -0.4072       | 0.6796       | 0.4899      | 0.042*     |
| C23  | -0.19191 (13) | 0.49357 (13) | 0.50166 (5) | 0.0280 (3) |
| H23A | -0.1551       | 0.5324       | 0.5259      | 0.042*     |
| H23B | -0.1334       | 0.4626       | 0.4824      | 0.042*     |
| H23C | -0.2396       | 0.4338       | 0.5131      | 0.042*     |
| C24  | 0.39966 (11)  | 0.46439 (12) | 0.35714 (5) | 0.0238 (3) |
| H24A | 0.4831        | 0.4594       | 0.3577      | 0.036*     |
| H24B | 0.3739        | 0.5160       | 0.3797      | 0.036*     |
| H24C | 0.3748        | 0.4908       | 0.3285      | 0.036*     |
| H14O | 0.3488 (19)   | 0.1956 (19)  | 0.4055 (8)  | 0.047 (6)* |

Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|----|------------|------------|------------|-------------|------------|-------------|
| O1 | 0.0129 (4) | 0.0191 (4) | 0.0165 (4) | -0.0030 (3) | 0.0024 (3) | -0.0032 (3) |

|     |            |            |            |             |             |             |
|-----|------------|------------|------------|-------------|-------------|-------------|
| O2  | 0.0224 (5) | 0.0237 (5) | 0.0223 (5) | -0.0030 (4) | 0.0075 (4)  | 0.0022 (4)  |
| O3  | 0.0185 (5) | 0.0247 (5) | 0.0339 (6) | -0.0067 (4) | 0.0031 (4)  | -0.0047 (4) |
| O4  | 0.0105 (4) | 0.0246 (5) | 0.0272 (5) | 0.0030 (3)  | 0.0023 (3)  | 0.0053 (4)  |
| O5  | 0.0165 (5) | 0.0195 (5) | 0.0315 (5) | 0.0044 (4)  | -0.0038 (4) | 0.0044 (4)  |
| C1  | 0.0140 (5) | 0.0146 (5) | 0.0152 (5) | 0.0022 (4)  | 0.0005 (4)  | 0.0006 (4)  |
| C2  | 0.0153 (5) | 0.0179 (5) | 0.0179 (6) | -0.0010 (4) | -0.0009 (4) | -0.0017 (5) |
| C3  | 0.0214 (6) | 0.0169 (6) | 0.0187 (6) | -0.0027 (5) | 0.0022 (5)  | -0.0026 (5) |
| C4  | 0.0263 (7) | 0.0216 (6) | 0.0166 (6) | -0.0029 (5) | 0.0036 (5)  | -0.0008 (5) |
| C5  | 0.0205 (6) | 0.0143 (5) | 0.0166 (6) | 0.0021 (4)  | 0.0024 (5)  | 0.0028 (5)  |
| C6  | 0.0132 (5) | 0.0135 (5) | 0.0159 (5) | 0.0021 (4)  | 0.0003 (4)  | 0.0024 (4)  |
| C7  | 0.0106 (5) | 0.0146 (5) | 0.0173 (6) | 0.0004 (4)  | 0.0012 (4)  | 0.0017 (4)  |
| C8  | 0.0114 (5) | 0.0148 (5) | 0.0166 (5) | 0.0015 (4)  | -0.0001 (4) | 0.0015 (4)  |
| C9  | 0.0144 (5) | 0.0166 (5) | 0.0206 (6) | 0.0004 (4)  | -0.0021 (5) | 0.0007 (5)  |
| C10 | 0.0165 (6) | 0.0202 (6) | 0.0219 (6) | -0.0002 (5) | -0.0008 (5) | -0.0049 (5) |
| C11 | 0.0155 (5) | 0.0237 (6) | 0.0163 (6) | -0.0008 (5) | 0.0010 (5)  | -0.0023 (5) |
| C12 | 0.0127 (5) | 0.0229 (6) | 0.0191 (6) | -0.0005 (4) | 0.0017 (4)  | -0.0036 (5) |
| C13 | 0.0119 (5) | 0.0161 (5) | 0.0156 (5) | 0.0006 (4)  | -0.0011 (4) | -0.0001 (5) |
| C14 | 0.0116 (5) | 0.0152 (5) | 0.0164 (5) | 0.0014 (4)  | -0.0005 (4) | -0.0004 (4) |
| C15 | 0.0129 (5) | 0.0156 (5) | 0.0164 (5) | -0.0004 (4) | 0.0002 (4)  | 0.0008 (4)  |
| C16 | 0.0112 (5) | 0.0199 (6) | 0.0151 (5) | 0.0013 (4)  | -0.0007 (4) | -0.0016 (5) |
| C17 | 0.0141 (5) | 0.0177 (6) | 0.0171 (6) | 0.0026 (4)  | -0.0031 (4) | -0.0001 (5) |
| C18 | 0.0169 (6) | 0.0173 (6) | 0.0235 (6) | -0.0005 (4) | -0.0003 (5) | 0.0043 (5)  |
| C19 | 0.0130 (5) | 0.0193 (6) | 0.0235 (6) | -0.0002 (4) | 0.0016 (5)  | 0.0028 (5)  |
| C20 | 0.0260 (7) | 0.0145 (6) | 0.0354 (8) | 0.0013 (5)  | 0.0065 (6)  | 0.0001 (6)  |
| C21 | 0.0334 (8) | 0.0288 (7) | 0.0252 (7) | -0.0090 (6) | 0.0034 (6)  | -0.0102 (6) |
| C22 | 0.0221 (7) | 0.0409 (8) | 0.0216 (7) | -0.0028 (6) | 0.0033 (5)  | -0.0115 (6) |
| C23 | 0.0301 (7) | 0.0339 (8) | 0.0200 (7) | 0.0016 (6)  | -0.0021 (6) | 0.0045 (6)  |
| C24 | 0.0143 (6) | 0.0272 (7) | 0.0298 (7) | -0.0045 (5) | 0.0002 (5)  | -0.0047 (6) |

*Geometric parameters (Å, °)*

|         |             |          |             |
|---------|-------------|----------|-------------|
| O1—C13  | 1.3772 (15) | C11—C22  | 1.5317 (18) |
| O1—C1   | 1.3802 (14) | C11—C23  | 1.5333 (19) |
| O2—C5   | 1.2263 (15) | C11—C12  | 1.5370 (18) |
| O3—C9   | 1.2246 (15) | C12—C13  | 1.4922 (17) |
| O4—C16  | 1.3714 (15) | C12—H12A | 0.9700      |
| O4—C24  | 1.4272 (17) | C12—H12B | 0.9700      |
| O5—C17  | 1.3591 (15) | C14—C19  | 1.3922 (18) |
| O5—H14O | 0.86 (2)    | C14—C15  | 1.4001 (16) |
| C1—C6   | 1.3427 (17) | C15—C16  | 1.3886 (17) |
| C1—C2   | 1.4924 (17) | C15—H15A | 0.9300      |
| C2—C3   | 1.5372 (18) | C16—C17  | 1.4007 (18) |
| C2—H2A  | 0.9700      | C17—C18  | 1.3867 (18) |
| C2—H2B  | 0.9700      | C18—C19  | 1.3877 (18) |
| C3—C21  | 1.5301 (19) | C18—H18A | 0.9300      |
| C3—C20  | 1.5329 (19) | C19—H19A | 0.9300      |
| C3—C4   | 1.5350 (18) | C20—H20A | 0.9600      |
| C4—C5   | 1.5106 (19) | C20—H20B | 0.9600      |



|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C4—H4A      | 0.9700      | C20—H20C      | 0.9600      |
| C4—H4B      | 0.9700      | C21—H21A      | 0.9600      |
| C5—C6       | 1.4730 (17) | C21—H21B      | 0.9600      |
| C6—C7       | 1.5140 (17) | C21—H21C      | 0.9600      |
| C7—C8       | 1.5108 (17) | C22—H22A      | 0.9600      |
| C7—C14      | 1.5278 (16) | C22—H22B      | 0.9600      |
| C7—H7A      | 0.9800      | C22—H22C      | 0.9600      |
| C8—C13      | 1.3454 (16) | C23—H23A      | 0.9600      |
| C8—C9       | 1.4706 (17) | C23—H23B      | 0.9600      |
| C9—C10      | 1.5143 (18) | C23—H23C      | 0.9600      |
| C10—C11     | 1.5317 (18) | C24—H24A      | 0.9600      |
| C10—H10A    | 0.9700      | C24—H24B      | 0.9600      |
| C10—H10B    | 0.9700      | C24—H24C      | 0.9600      |
|             |             |               |             |
| C13—O1—C1   | 117.88 (9)  | C11—C12—H12A  | 109.1       |
| C16—O4—C24  | 117.15 (10) | C13—C12—H12B  | 109.1       |
| C17—O5—H14O | 110.3 (15)  | C11—C12—H12B  | 109.1       |
| C6—C1—O1    | 122.11 (11) | H12A—C12—H12B | 107.8       |
| C6—C1—C2    | 126.34 (11) | C8—C13—O1     | 122.80 (11) |
| O1—C1—C2    | 111.55 (10) | C8—C13—C12    | 125.88 (11) |
| C1—C2—C3    | 111.36 (10) | O1—C13—C12    | 111.32 (10) |
| C1—C2—H2A   | 109.4       | C19—C14—C15   | 118.86 (11) |
| C3—C2—H2A   | 109.4       | C19—C14—C7    | 119.92 (10) |
| C1—C2—H2B   | 109.4       | C15—C14—C7    | 120.94 (11) |
| C3—C2—H2B   | 109.4       | C16—C15—C14   | 120.35 (12) |
| H2A—C2—H2B  | 108.0       | C16—C15—H15A  | 119.8       |
| C21—C3—C20  | 109.88 (12) | C14—C15—H15A  | 119.8       |
| C21—C3—C4   | 109.24 (11) | O4—C16—C15    | 125.52 (12) |
| C20—C3—C4   | 110.30 (11) | O4—C16—C17    | 114.24 (11) |
| C21—C3—C2   | 109.31 (11) | C15—C16—C17   | 120.23 (11) |
| C20—C3—C2   | 110.83 (11) | O5—C17—C18    | 118.62 (12) |
| C4—C3—C2    | 107.22 (10) | O5—C17—C16    | 122.09 (11) |
| C5—C4—C3    | 113.79 (11) | C18—C17—C16   | 119.28 (11) |
| C5—C4—H4A   | 108.8       | C17—C18—C19   | 120.37 (12) |
| C3—C4—H4A   | 108.8       | C17—C18—H18A  | 119.8       |
| C5—C4—H4B   | 108.8       | C19—C18—H18A  | 119.8       |
| C3—C4—H4B   | 108.8       | C18—C19—C14   | 120.78 (12) |
| H4A—C4—H4B  | 107.7       | C18—C19—H19A  | 119.6       |
| O2—C5—C6    | 120.71 (12) | C14—C19—H19A  | 119.6       |
| O2—C5—C4    | 121.91 (12) | C3—C20—H20A   | 109.5       |
| C6—C5—C4    | 117.36 (11) | C3—C20—H20B   | 109.5       |
| C1—C6—C5    | 118.29 (11) | H20A—C20—H20B | 109.5       |
| C1—C6—C7    | 122.20 (11) | C3—C20—H20C   | 109.5       |
| C5—C6—C7    | 119.31 (10) | H20A—C20—H20C | 109.5       |
| C8—C7—C6    | 108.21 (10) | H20B—C20—H20C | 109.5       |
| C8—C7—C14   | 112.65 (10) | C3—C21—H21A   | 109.5       |
| C6—C7—C14   | 107.84 (10) | C3—C21—H21B   | 109.5       |
| C8—C7—H7A   | 109.4       | H21A—C21—H21B | 109.5       |

|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C6—C7—H7A     | 109.4        | C3—C21—H21C     | 109.5        |
| C14—C7—H7A    | 109.4        | H21A—C21—H21C   | 109.5        |
| C13—C8—C9     | 118.22 (11)  | H21B—C21—H21C   | 109.5        |
| C13—C8—C7     | 121.72 (11)  | C11—C22—H22A    | 109.5        |
| C9—C8—C7      | 120.07 (10)  | C11—C22—H22B    | 109.5        |
| O3—C9—C8      | 121.30 (12)  | H22A—C22—H22B   | 109.5        |
| O3—C9—C10     | 120.51 (12)  | C11—C22—H22C    | 109.5        |
| C8—C9—C10     | 118.14 (11)  | H22A—C22—H22C   | 109.5        |
| C9—C10—C11    | 114.09 (11)  | H22B—C22—H22C   | 109.5        |
| C9—C10—H10A   | 108.7        | C11—C23—H23A    | 109.5        |
| C11—C10—H10A  | 108.7        | C11—C23—H23B    | 109.5        |
| C9—C10—H10B   | 108.7        | H23A—C23—H23B   | 109.5        |
| C11—C10—H10B  | 108.7        | C11—C23—H23C    | 109.5        |
| H10A—C10—H10B | 107.6        | H23A—C23—H23C   | 109.5        |
| C22—C11—C10   | 110.04 (11)  | H23B—C23—H23C   | 109.5        |
| C22—C11—C23   | 109.54 (12)  | O4—C24—H24A     | 109.5        |
| C10—C11—C23   | 109.87 (11)  | O4—C24—H24B     | 109.5        |
| C22—C11—C12   | 108.88 (10)  | H24A—C24—H24B   | 109.5        |
| C10—C11—C12   | 107.80 (11)  | O4—C24—H24C     | 109.5        |
| C23—C11—C12   | 110.68 (11)  | H24A—C24—H24C   | 109.5        |
| C13—C12—C11   | 112.46 (10)  | H24B—C24—H24C   | 109.5        |
| C13—C12—H12A  | 109.1        |                 |              |
|               |              |                 |              |
| C13—O1—C1—C6  | 10.47 (17)   | C9—C10—C11—C22  | -172.25 (11) |
| C13—O1—C1—C2  | -169.61 (10) | C9—C10—C11—C23  | 67.06 (14)   |
| C6—C1—C2—C3   | 22.80 (18)   | C9—C10—C11—C12  | -53.64 (14)  |
| O1—C1—C2—C3   | -157.11 (10) | C22—C11—C12—C13 | 167.54 (12)  |
| C1—C2—C3—C21  | -168.27 (11) | C10—C11—C12—C13 | 48.19 (14)   |
| C1—C2—C3—C20  | 70.47 (13)   | C23—C11—C12—C13 | -71.99 (14)  |
| C1—C2—C3—C4   | -49.96 (14)  | C9—C8—C13—O1    | 174.91 (11)  |
| C21—C3—C4—C5  | 174.64 (12)  | C7—C8—C13—O1    | -5.31 (18)   |
| C20—C3—C4—C5  | -64.49 (15)  | C9—C8—C13—C12   | -4.82 (19)   |
| C2—C3—C4—C5   | 56.29 (14)   | C7—C8—C13—C12   | 174.95 (12)  |
| C3—C4—C5—O2   | 148.98 (12)  | C1—O1—C13—C8    | -12.05 (17)  |
| C3—C4—C5—C6   | -32.87 (16)  | C1—O1—C13—C12   | 167.72 (10)  |
| O1—C1—C6—C5   | -176.84 (10) | C11—C12—C13—C8  | -21.12 (18)  |
| C2—C1—C6—C5   | 3.25 (18)    | C11—C12—C13—O1  | 159.11 (10)  |
| O1—C1—C6—C7   | 8.37 (18)    | C8—C7—C14—C19   | 52.88 (15)   |
| C2—C1—C6—C7   | -171.54 (11) | C6—C7—C14—C19   | -66.46 (15)  |
| O2—C5—C6—C1   | 179.82 (11)  | C8—C7—C14—C15   | -133.24 (12) |
| C4—C5—C6—C1   | 1.65 (17)    | C6—C7—C14—C15   | 107.43 (13)  |
| O2—C5—C6—C7   | -5.23 (17)   | C19—C14—C15—C16 | 2.08 (19)    |
| C4—C5—C6—C7   | 176.59 (11)  | C7—C14—C15—C16  | -171.87 (11) |
| C1—C6—C7—C8   | -22.67 (15)  | C24—O4—C16—C15  | 25.08 (18)   |
| C5—C6—C7—C8   | 162.59 (10)  | C24—O4—C16—C17  | -156.10 (12) |
| C1—C6—C7—C14  | 99.45 (13)   | C14—C15—C16—O4  | 179.50 (12)  |
| C5—C6—C7—C14  | -75.29 (13)  | C14—C15—C16—C17 | 0.74 (19)    |
| C6—C7—C8—C13  | 21.08 (15)   | O4—C16—C17—O5   | -1.71 (18)   |

|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C14—C7—C8—C13 | -98.04 (13)  | C15—C16—C17—O5  | 177.18 (12)  |
| C6—C7—C8—C9   | -159.15 (11) | O4—C16—C17—C18  | 177.85 (12)  |
| C14—C7—C8—C9  | 81.73 (14)   | C15—C16—C17—C18 | -3.26 (19)   |
| C13—C8—C9—O3  | -177.09 (12) | O5—C17—C18—C19  | -177.48 (12) |
| C7—C8—C9—O3   | 3.13 (18)    | C16—C17—C18—C19 | 3.0 (2)      |
| C13—C8—C9—C10 | 0.12 (17)    | C17—C18—C19—C14 | -0.1 (2)     |
| C7—C8—C9—C10  | -179.65 (11) | C15—C14—C19—C18 | -2.4 (2)     |
| O3—C9—C10—C11 | -152.16 (12) | C7—C14—C19—C18  | 171.61 (12)  |
| C8—C9—C10—C11 | 30.60 (16)   |                 |              |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i>      | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| O5—H14O...O3 <sup>i</sup>    | 0.86 (2)    | 1.95 (2)      | 2.7319 (13)           | 151 (2)                 |
| C2—H2A...O2 <sup>ii</sup>    | 0.97        | 2.55          | 3.5003 (16)           | 165                     |
| C20—H20C...O2 <sup>iii</sup> | 0.96        | 2.58          | 3.4646 (17)           | 154                     |

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