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# 2,7-Dihydroxy-3,6-dimethoxyphenanthrene from *Dehaasia longipedicellata*

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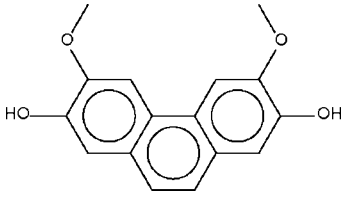
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.046; $wR$ factor = 0.150; data-to-parameter ratio = 12.6.

The hydroxy groups in the title compound, $C_{16}H_{14}O_4$, are each hydrogen bonded to the adjacent methoxy O atom; one of the two hydroxy groups is additionally linked to the O atom of the methoxy group of another molecule, forming a linear chain.

## Related literature

For related compounds isolated from other plants, see: Bhandari *et al.* (1985); Mujumder *et al.* (1985); Theuns *et al.* (1985); Zurinah Mahmud *et al.* (1992). For the crystal structure of 2,3-dimethoxy-6,7-methylenedioxyphenanthrene, see: Wang *et al.* (2007).




## Experimental

### *Crystal data*

$C_{16}H_{14}O_4$
$M_r$ = 270.27
Monoclinic, $P2_1/c$
$a$ = 11.6268 (2) Å
$b$ = 7.2207 (1) Å
$c$ = 16.5351 (2) Å
$\beta$ = 109.196 (1)°
$V$ = 1311.00 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 100 (2) K
0.30 × 0.25 × 0.05 mm

### *Data collection*

Bruker SMART APEX diffractometer
Absorption correction: none
15710 measured reflections
2991 independent reflections
2671 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.150
$S$ = 1.10
2991 reflections
237 parameters
14 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.42 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2o···O1 | 0.85 (1) | 2.20 (3) | 2.670 (2) | 115 (2) |
| O2—H2o···O3$^{i}$ | 0.85 (1) | 1.95 (1) | 2.754 (2) | 159 (3) |
| O3—H3o···O4 | 0.85 (1) | 2.08 (3) | 2.614 (2) | 121 (3) |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2712).

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# supporting information

*Acta Cryst.* (2008). E**64**, o1135 [doi:10.1107/S1600536808014451]

## 2,7-Dihydroxy-3,6-dimethoxyphenanthrene from *Dehaasia longipedicellata*

**Mat Ropi Mukhtar, Mohd Azlan Nafiah, Khalijah Awang, A. Hamid A. Hadi and Seik Weng Ng**

### S1. Comment

2,7-Dihydroxy-3,6-dimethoxylphenanthrene (Scheme I, Fig. 1) is a new compound isolated from *Dehaasia longipedicellata* (Ridl.) Kosterm. The hydroxy groups are each hydrogen-bonded to the adjacent methoxy oxygen; one of the two hydroxy groups is additionally linked to the oxygen atom of the methoxy group of another molecule to form a linear chain.

### S2. Experimental

*Dehaasia longipedicellata* (Ridl.) Kosterm. was collected in Raub Forest Reserve, Pahang, Malaysia, in 1997. Specimens (KL4719) were deposited at the herbarium, Department of Chemistry, University of Malaya and the herbarium of the Forest Research Institute of Malaysia.

Some 1.4 kg of dried and ground leaves of *D. longipedicellata* was extracted with dichloromethane. The dichloromethane extract was concentrated under reduced pressure to a volume of 500 ml. This was repeatedly extracted with a solution of 5% hydrochloric acid. The combined extracts were then basified with 10% ammonium hydroxide to pH 11 and then re-extracted with dichloromethane. The brown alkaloid fraction amounted to (8.83 g). A portion (3 g) was subjected to column chromatography on silica gel 60 $GF_{254}$ by using a step gradient of dichloromethane and methanol. The separation afforded 15 fractions, the first (100% dichloromethane) gave 2,7-dihydroxy-3,6-dimethoxyphenanthrene (8 mg), whose formulation was established by spectroscopic analysis. Light brown prisms were obtained upon recrystallization from dichloromethane.

### S3. Refinement

Hydrogen atoms were located in a difference Fourier map. They were refined isotropically with distance restraints of C–H 0.95±0.01 Å and O–H 0.85±0.01 Å.

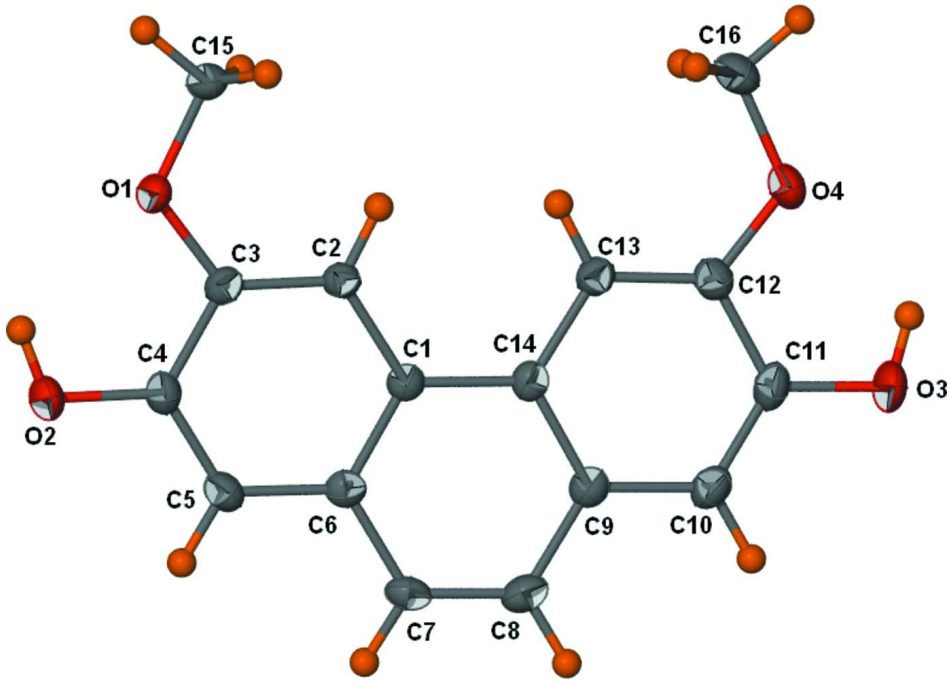


**Figure 1**

Displacement ellipsoid plot (Barbour, 2001) of the molecule of $C_{16}H_{16}O_4$ drawn at the 70% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

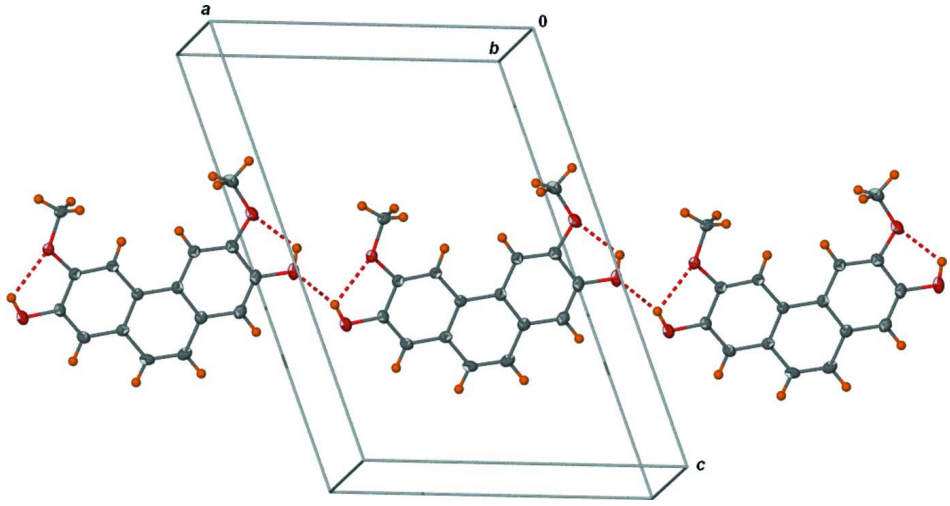


**Figure 2**

Hydrogen-bonded chain structure.

### 2,7-Dihydroxy-3,6-dimethoxyphenanthrene

*Crystal data*

$C_{16}H_{14}O_4$
$M_r = 270.27$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.6268$ (2) Å
$b = 7.2207$ (1) Å
$c = 16.5351$ (2) Å
$\beta = 109.196$ (1)°
$V = 1311.00$ (3) Å$^3$
$Z = 4$

$F(000) = 568$
$D_x = 1.369$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8700 reflections
$\theta = 2.6$–$28.3°$
$\mu = 0.10$ mm$^{-1}$
$T = 100$ K
Prism, pale brown
0.30 × 0.25 × 0.05 mm

*Data collection*

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
15710 measured reflections
2991 independent reflections
2671 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
$h = -11 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 21$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.150$
$S = 1.11$
2991 reflections
237 parameters
14 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.2422P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å$^{-3}$
$\Delta\rho_{min} = -0.23$ e Å$^{-3}$

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.71900 (10) | 0.23952 (17) | 0.51347 (7) | 0.0175 (3) |
| O2 | 0.85160 (11) | 0.40262 (19) | 0.65922 (8) | 0.0213 (3) |
| O3 | −0.02829 (12) | 0.2974 (2) | 0.54817 (9) | 0.0277 (3) |
| O4 | 0.05316 (11) | 0.19182 (19) | 0.42576 (8) | 0.0236 (3) |
| C1 | 0.47440 (14) | 0.3578 (2) | 0.60344 (10) | 0.0137 (3) |
| C2 | 0.53118 (14) | 0.2890 (2) | 0.54541 (10) | 0.0141 (3) |
| C3 | 0.65507 (14) | 0.3029 (2) | 0.56408 (10) | 0.0147 (3) |
| C4 | 0.72887 (14) | 0.3887 (2) | 0.64087 (10) | 0.0160 (3) |
| C5 | 0.67565 (15) | 0.4568 (2) | 0.69713 (10) | 0.0164 (3) |
| C6 | 0.54872 (14) | 0.4405 (2) | 0.68039 (10) | 0.0148 (3) |
| C7 | 0.49473 (15) | 0.5060 (2) | 0.74130 (10) | 0.0161 (3) |
| C8 | 0.37442 (15) | 0.4861 (2) | 0.72813 (10) | 0.0174 (3) |
| C9 | 0.29560 (15) | 0.4047 (2) | 0.65046 (10) | 0.0159 (3) |
| C10 | 0.16910 (16) | 0.3874 (2) | 0.63624 (11) | 0.0197 (4) |
| C11 | 0.09423 (15) | 0.3145 (2) | 0.56196 (11) | 0.0197 (4) |
| C12 | 0.14106 (15) | 0.2572 (2) | 0.49676 (11) | 0.0180 (3) |
| C13 | 0.26312 (15) | 0.2727 (2) | 0.50896 (10) | 0.0157 (3) |
| C14 | 0.34417 (14) | 0.3444 (2) | 0.58698 (10) | 0.0142 (3) |
| C15 | 0.64950 (15) | 0.1659 (2) | 0.43192 (10) | 0.0172 (3) |
| C16 | 0.09098 (17) | 0.1296 (3) | 0.35617 (11) | 0.0234 (4) |
| H2O | 0.870 (2) | 0.361 (4) | 0.6173 (12) | 0.042 (7)* |

| | | | | |
|---|---|---|---|---|
| H3O | −0.059 (3) | 0.257 (4) | 0.4974 (10) | 0.060 (9)* |
| H2 | 0.4840 (17) | 0.236 (3) | 0.4925 (9) | 0.019 (5)* |
| H5 | 0.7270 (16) | 0.513 (3) | 0.7485 (9) | 0.019 (5)* |
| H7 | 0.5458 (16) | 0.571 (3) | 0.7897 (10) | 0.019 (5)* |
| H8 | 0.3392 (18) | 0.525 (3) | 0.7698 (11) | 0.019 (5)* |
| H10 | 0.1355 (19) | 0.429 (3) | 0.6789 (11) | 0.027 (6)* |
| H13 | 0.2932 (18) | 0.230 (3) | 0.4656 (10) | 0.019 (5)* |
| H151 | 0.7096 (16) | 0.132 (3) | 0.4069 (14) | 0.028 (6)* |
| H152 | 0.5945 (16) | 0.259 (2) | 0.4015 (12) | 0.019 (5)* |
| H153 | 0.6033 (16) | 0.058 (2) | 0.4361 (13) | 0.015 (5)* |
| H161 | 0.0189 (14) | 0.090 (3) | 0.3123 (11) | 0.030 (6)* |
| H162 | 0.1507 (18) | 0.034 (3) | 0.3737 (15) | 0.034 (6)* |
| H163 | 0.128 (2) | 0.234 (2) | 0.3382 (15) | 0.032 (6)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0127 (5) | 0.0242 (6) | 0.0160 (6) | 0.0004 (4) | 0.0053 (4) | −0.0032 (4) |
| O2 | 0.0122 (6) | 0.0314 (7) | 0.0193 (6) | −0.0021 (5) | 0.0038 (4) | −0.0035 (5) |
| O3 | 0.0126 (6) | 0.0442 (8) | 0.0273 (7) | −0.0017 (5) | 0.0079 (5) | −0.0053 (6) |
| O4 | 0.0135 (6) | 0.0342 (7) | 0.0207 (6) | −0.0026 (5) | 0.0025 (5) | −0.0061 (5) |
| C1 | 0.0140 (7) | 0.0133 (7) | 0.0138 (7) | 0.0008 (6) | 0.0046 (6) | 0.0016 (5) |
| C2 | 0.0148 (7) | 0.0151 (7) | 0.0122 (7) | 0.0001 (6) | 0.0039 (6) | 0.0004 (5) |
| C3 | 0.0152 (7) | 0.0153 (7) | 0.0143 (7) | 0.0014 (6) | 0.0058 (6) | 0.0013 (6) |
| C4 | 0.0126 (7) | 0.0174 (7) | 0.0171 (7) | −0.0008 (6) | 0.0037 (6) | 0.0023 (6) |
| C5 | 0.0164 (8) | 0.0169 (7) | 0.0137 (7) | −0.0017 (6) | 0.0019 (6) | −0.0004 (6) |
| C6 | 0.0163 (8) | 0.0145 (7) | 0.0132 (7) | 0.0009 (6) | 0.0043 (6) | 0.0023 (5) |
| C7 | 0.0199 (8) | 0.0154 (7) | 0.0111 (7) | 0.0007 (6) | 0.0027 (6) | −0.0002 (5) |
| C8 | 0.0216 (8) | 0.0177 (7) | 0.0148 (7) | 0.0033 (6) | 0.0086 (6) | 0.0013 (6) |
| C9 | 0.0157 (8) | 0.0165 (7) | 0.0160 (7) | 0.0024 (6) | 0.0061 (6) | 0.0028 (6) |
| C10 | 0.0175 (8) | 0.0242 (8) | 0.0197 (8) | 0.0028 (6) | 0.0094 (6) | 0.0010 (6) |
| C11 | 0.0129 (8) | 0.0243 (8) | 0.0231 (8) | 0.0019 (6) | 0.0076 (6) | 0.0029 (7) |
| C12 | 0.0154 (8) | 0.0197 (8) | 0.0173 (8) | 0.0000 (6) | 0.0033 (6) | −0.0002 (6) |
| C13 | 0.0156 (8) | 0.0176 (7) | 0.0146 (7) | 0.0011 (6) | 0.0059 (6) | 0.0013 (6) |
| C14 | 0.0136 (7) | 0.0138 (7) | 0.0152 (7) | 0.0017 (5) | 0.0048 (6) | 0.0026 (6) |
| C15 | 0.0181 (8) | 0.0198 (8) | 0.0142 (7) | 0.0003 (6) | 0.0061 (6) | −0.0021 (6) |
| C16 | 0.0197 (8) | 0.0295 (9) | 0.0177 (8) | −0.0019 (7) | 0.0016 (6) | −0.0054 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C3 | 1.3679 (19) | C7—C8 | 1.351 (2) |
| O1—C15 | 1.4273 (19) | C7—H7 | 0.949 (10) |
| O2—C4 | 1.3615 (19) | C8—C9 | 1.436 (2) |
| O2—H2O | 0.848 (10) | C8—H8 | 0.951 (9) |
| O3—C11 | 1.372 (2) | C9—C10 | 1.417 (2) |
| O3—H3O | 0.849 (10) | C9—C14 | 1.414 (2) |
| O4—C12 | 1.363 (2) | C10—C11 | 1.357 (2) |
| O4—C16 | 1.432 (2) | C10—H10 | 0.959 (10) |

| | | | |
|---|---|---|---|
| C1—C6 | 1.414 (2) | C11—C12 | 1.420 (2) |
| C1—C2 | 1.421 (2) | C12—C13 | 1.371 (2) |
| C1—C14 | 1.451 (2) | C13—C14 | 1.422 (2) |
| C2—C3 | 1.374 (2) | C13—H13 | 0.946 (9) |
| C2—H2 | 0.947 (9) | C15—H151 | 0.954 (10) |
| C3—C4 | 1.420 (2) | C15—H152 | 0.948 (9) |
| C4—C5 | 1.367 (2) | C15—H153 | 0.959 (9) |
| C5—C6 | 1.414 (2) | C16—H161 | 0.955 (10) |
| C5—H5 | 0.954 (9) | C16—H162 | 0.952 (10) |
| C6—C7 | 1.431 (2) | C16—H163 | 0.959 (10) |

| | | | |
|---|---|---|---|
| C3—O1—C15 | 116.73 (12) | C10—C9—C8 | 120.47 (15) |
| C4—O2—H2O | 108.9 (19) | C14—C9—C8 | 119.79 (14) |
| C11—O3—H3O | 105 (2) | C11—C10—C9 | 120.43 (15) |
| C12—O4—C16 | 117.34 (13) | C11—C10—H10 | 119.4 (14) |
| C6—C1—C2 | 118.23 (14) | C9—C10—H10 | 120.1 (14) |
| C6—C1—C14 | 119.23 (14) | C10—C11—O3 | 120.48 (16) |
| C2—C1—C14 | 122.54 (14) | C10—C11—C12 | 120.56 (15) |
| C3—C2—C1 | 120.55 (14) | O3—C11—C12 | 118.95 (15) |
| C3—C2—H2 | 118.9 (13) | O4—C12—C13 | 127.02 (15) |
| C1—C2—H2 | 120.6 (13) | O4—C12—C11 | 112.88 (15) |
| O1—C3—C2 | 125.36 (14) | C13—C12—C11 | 120.09 (15) |
| O1—C3—C4 | 113.75 (14) | C12—C13—C14 | 120.56 (15) |
| C2—C3—C4 | 120.89 (14) | C12—C13—H13 | 119.0 (13) |
| O2—C4—C5 | 119.84 (15) | C14—C13—H13 | 120.4 (13) |
| O2—C4—C3 | 120.83 (14) | C9—C14—C13 | 118.58 (14) |
| C5—C4—C3 | 119.33 (15) | C9—C14—C1 | 119.15 (14) |
| C4—C5—C6 | 120.91 (15) | C13—C14—C1 | 122.27 (14) |
| C4—C5—H5 | 117.9 (13) | O1—C15—H151 | 103.7 (14) |
| C6—C5—H5 | 121.1 (13) | O1—C15—H152 | 108.2 (13) |
| C5—C6—C1 | 120.07 (14) | H151—C15—H152 | 114.5 (19) |
| C5—C6—C7 | 120.38 (14) | O1—C15—H153 | 112.9 (12) |
| C1—C6—C7 | 119.55 (14) | H151—C15—H153 | 109.3 (19) |
| C8—C7—C6 | 121.47 (15) | H152—C15—H153 | 108.3 (18) |
| C8—C7—H7 | 121.1 (13) | O4—C16—H161 | 106.3 (14) |
| C6—C7—H7 | 117.4 (13) | O4—C16—H162 | 111.6 (15) |
| C7—C8—C9 | 120.69 (15) | H161—C16—H162 | 112 (2) |
| C7—C8—H8 | 121.4 (13) | O4—C16—H163 | 106.8 (15) |
| C9—C8—H8 | 117.9 (13) | H161—C16—H163 | 112 (2) |
| C10—C9—C14 | 119.73 (15) | H162—C16—H163 | 108 (2) |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | 0.0 (2) | C14—C9—C10—C11 | −0.4 (2) |
| C14—C1—C2—C3 | −179.27 (14) | C8—C9—C10—C11 | 178.42 (16) |
| C15—O1—C3—C2 | 5.0 (2) | C9—C10—C11—O3 | 179.88 (15) |
| C15—O1—C3—C4 | −174.81 (13) | C9—C10—C11—C12 | −1.0 (3) |
| C1—C2—C3—O1 | 179.19 (14) | C16—O4—C12—C13 | 0.9 (3) |
| C1—C2—C3—C4 | −1.0 (2) | C16—O4—C12—C11 | −179.78 (15) |
| O1—C3—C4—O2 | −0.1 (2) | C10—C11—C12—O4 | −178.39 (16) |

| | | | |
|---|---|---|---|
| C2—C3—C4—O2 | −179.89 (14) | O3—C11—C12—O4 | 0.7 (2) |
| O1—C3—C4—C5 | −179.60 (14) | C10—C11—C12—C13 | 1.0 (3) |
| C2—C3—C4—C5 | 0.6 (2) | O3—C11—C12—C13 | −179.95 (15) |
| O2—C4—C5—C6 | −178.64 (14) | O4—C12—C13—C14 | 179.82 (16) |
| C3—C4—C5—C6 | 0.9 (2) | C11—C12—C13—C14 | 0.6 (2) |
| C4—C5—C6—C1 | −1.9 (2) | C10—C9—C14—C13 | 1.9 (2) |
| C4—C5—C6—C7 | 177.63 (15) | C8—C9—C14—C13 | −176.96 (14) |
| C2—C1—C6—C5 | 1.4 (2) | C10—C9—C14—C1 | −178.18 (14) |
| C14—C1—C6—C5 | −179.26 (14) | C8—C9—C14—C1 | 3.0 (2) |
| C2—C1—C6—C7 | −178.10 (14) | C12—C13—C14—C9 | −1.9 (2) |
| C14—C1—C6—C7 | 1.2 (2) | C12—C13—C14—C1 | 178.09 (15) |
| C5—C6—C7—C8 | −177.65 (15) | C6—C1—C14—C9 | −3.6 (2) |
| C1—C6—C7—C8 | 1.9 (2) | C2—C1—C14—C9 | 175.69 (14) |
| C6—C7—C8—C9 | −2.5 (2) | C6—C1—C14—C13 | 176.38 (14) |
| C7—C8—C9—C10 | −178.78 (15) | C2—C1—C14—C13 | −4.3 (2) |
| C7—C8—C9—C14 | 0.0 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2o···O1 | 0.85 (1) | 2.20 (3) | 2.670 (2) | 115 (2) |
| O2—H2o···O3$^{i}$ | 0.85 (1) | 1.95 (1) | 2.754 (2) | 159 (3) |
| O3—H3o···O4 | 0.85 (1) | 2.08 (3) | 2.614 (2) | 121 (3) |

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