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3-Allyl-2-hydroxy-5,6,8-trimethoxy-naphthalene-1,4-dione

Dominea C. K. Rathwell, Kit Y. Tsang, Ka Wai Choi, Peter D. W. Boyd and Margaret A. Brimble*

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand
Correspondence e-mail: m.brimble@auckland.ac.nz

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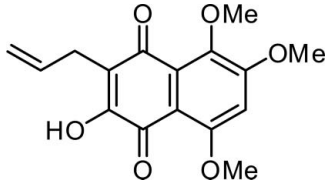
Key indicators: single-crystal X-ray study; T = 89 K; mean σ(C–C) = 0.003 Å; R factor = 0.040; wR factor = 0.086; data-to-parameter ratio = 9.6.

In the crystal structure of the title compound, $C_{16}H_{16}O_6$, a pair of naphthoquinone rings are linked *via* O—H···O—C hydrogen bonds in a nearly orthogonal arrangement. This dimeric unit is linked to a neighbouring dimer by π–π stacking interactions between the naphthoquinone rings, where the distance between the mean plane of the naphtoquinone backbones is 3.468 Å, and O—H···O—C hydrogen bonds.

Related literature

For details of the synthesis, see: Brimble *et al.* (2008). For related syntheses, see: Reissig *et al.* (2006); Kozlowski *et al.* (2008). For the biological activity of rubromycins, see: Brockmann *et al.* (1953, 1966).



Experimental

Crystal data

$C_{16}H_{16}O_6$
M_r = 304.29
Orthorhombic, $P2_12_12_1$
a = 4.68110 (10) Å
b = 12.6577 (3) Å
c = 23.3392 (5) Å
V = 1382.89 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 89 (2) K
0.28 × 0.09 × 0.06 mm

Data collection

Bruker SMART diffractometer with APEXII CCD detector
Absorption correction: none
14372 measured reflections
1914 independent reflections
1415 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.085
S = 1.09
1914 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O16—H16···O12	0.82	2.14	2.612 (2)	117
O16—H16···O12^{i}	0.82	2.05	2.777 (2)	148
O16—H16···O19^{i}	0.82	2.40	2.926 (2)	122

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2008).

The authors thank Tania Groutso for her help with the data collection and the New Zealand Tertiary Education Commission for the award of Bright Future Top Achiever Doctoral Scholarships (DCKR and KYT).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2489).

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supporting information

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3-Allyl-2-hydroxy-5,6,8-trimethoxynaphthalene-1,4-dione

Dominea C. K. Rathwell, Kit Y. Tsang, Ka Wai Choi, Peter D. W. Boyd and Margaret A. Brimble

S1. Comment

The rubromycins are a structurally related family of antibiotics that exhibit a wide range of biological activity (Brockmann *et al.*, 1953, 1966). The common structural features of this family of antibiotics consists of a naphthoquinone and an isocoumarin ring linked through a bis-benzannelated-5,6-spiroacetal ring system. Our recent synthetic efforts have focused on the synthesis of the naphthoquinone units of the rubromycins and its regioisomeric counterpart. The tandem Ullman coupling–Claisen rearrangement has been successfully employed to access the regioisomeric naphthoquinones in which the title compound was isolated as a minor isomer. The newly introduced hydroxyl and allyl groups were established by X-ray crystallography to be at C8 and C9, respectively (Fig. 1). The crystal packing is dominated by intermolecular hydrogen bonds and π–π interactions (Table 1, Fig. 2). Further detailed analysis revealed that a pair of naphthoquinone rings are linked *via* O—H···O—C hydrogen bonding in a near orthogonal arrangement with respect to each other. This dimeric unit stacks on top of a neighbouring dimer with π–π stacking interactions between the naphthoquinone rings and O—H···O—C hydrogen bonding (Table 1, Fig. 2).

S2. Experimental

A mixture of 2-bromo-5,7,8-trimethoxynaphthalene-1,4-dione (500 mg, 1.6 mmol), allyl alcohol (0.5 ml, 10 mmol), copper iodide (46 mg, 0.14 mmol) and caesium carbonate (940 mg, 2.9 mmol) in toluene (3 ml) was heated at 320 K under a nitrogen atmosphere in a sealed tube for 30 min. After allowing the mixture to cool to room temperature, the brownish mixture was filtered through a plug of Celite. The brown filtrate was then irradiated with microwave at 410 K (60 W) for 180 min in a sealed tube (10 ml pressure-rated reaction vial) in a self-tuning single mode irradiating synthesizer (CEM Discover LabMate microwave synthesizer). The resulting solution was then concentrated *in vacuo* to afford a brown residue. Purification of the crude residue by flash column chromatography using ethyl acetate–hexane (2:8) with gradient elution to neat ethyl acetate afforded the title compound (116 mg, 24%) as a yellow solid. Recrystallization from acetonitrile afforded yellow needles suitable for X-ray diffraction. m.p. 427–431 K

S3. Refinement

Hydrogen atoms were placed in calculated positions and refined using the riding model (C—H 0.93–0.97 Å), with U_{iso}(H) = 1.5 times U_{eq}(O) and U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

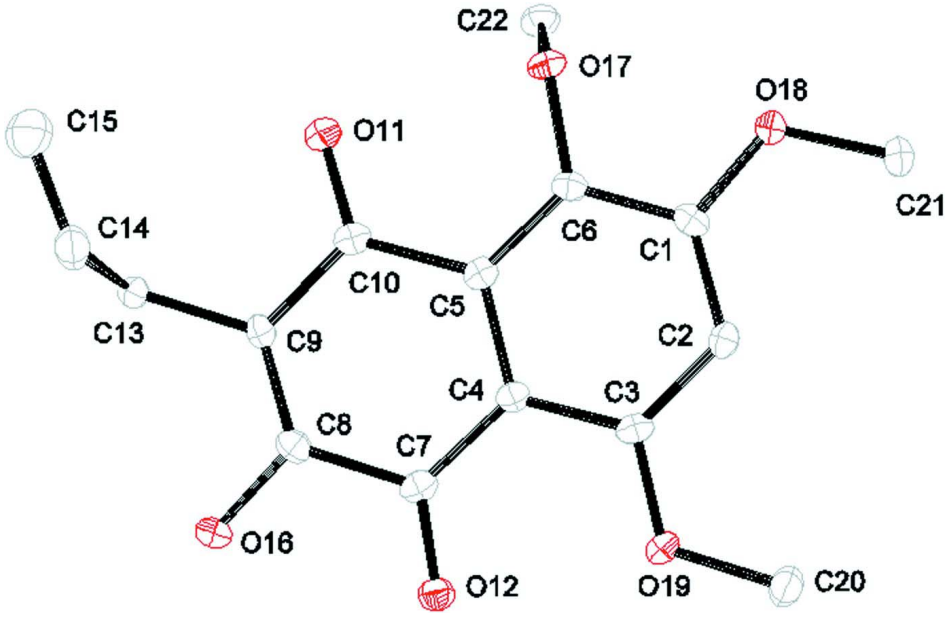

Figure 1

The molecular structure and the atom numbering scheme of the title compound. Ellipsoids are drawn at 50% probability level for non-H atoms.

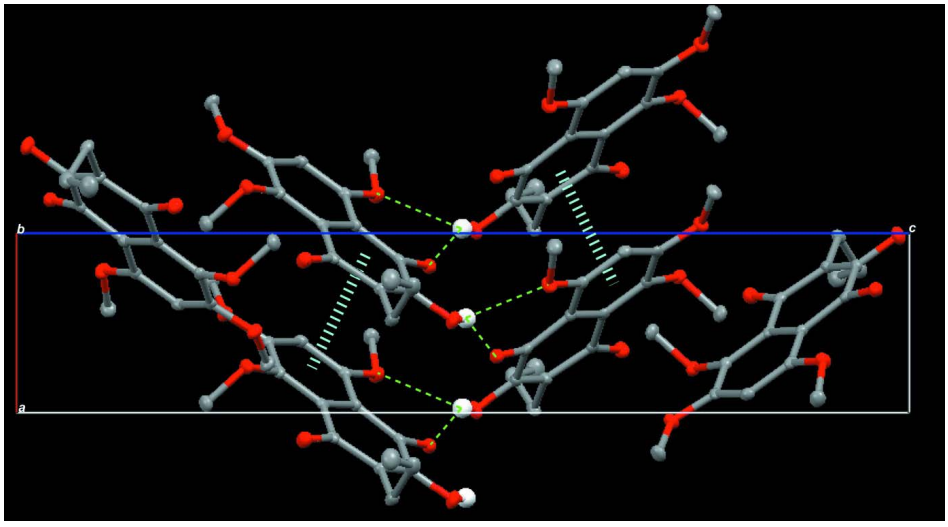

Figure 2

Molecular packing of the title naphthoquinone, viewed along the *b* axis. (···, in green) hydrogen bond; (|||, in blue) π–π interaction. The H atoms not involved in hydrogen bonding have been omitted.

3-Allyl-2-hydroxy-5,6,8-trimethoxynaphthalene-1,4-dione

Crystal data

$C_{16}H_{16}O_6$
$M_r = 304.29$
Orthorhombic, $P2_12_12_1$
$a = 4.6811\ (1)$ Å
$b = 12.6577\ (3)$ Å
$c = 23.3392\ (5)$ Å
$V = 1382.89\ (5)$ Å^3
$Z = 4$
$F(000) = 640$
$D_x = 1.462$ Mg m^{-3}

Melting point: 429(2) K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3251 reflections
θ = 1.8–27.9°
μ = 0.11 mm^{-1}
T = 89 K
Needle, yellow
0.28 × 0.09 × 0.06 mm

Data collection

Bruker SMART diffractometer with APEXII CCD detector
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
14372 measured reflections
1914 independent reflections
1415 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.9°, θ_{min} = 1.8°
h = −6→4
k = −16→16
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.085
S = 1.09
1914 reflections
200 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.1796P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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}
O16	−0.4858 (4)	0.07396 (13)	0.01234 (6)	0.0192 (4)
H16	−0.4751	0.1330	−0.0020	0.029*
O11	−0.1507 (4)	−0.09214 (12)	0.17755 (7)	0.0183 (4)
O17	0.2562 (4)	−0.00627 (12)	0.24216 (6)	0.0150 (4)
O19	0.2115 (4)	0.33797 (12)	0.09662 (7)	0.0174 (4)
O12	−0.1853 (4)	0.24133 (13)	0.03789 (6)	0.0164 (4)
O18	0.5482 (4)	0.16101 (12)	0.26649 (6)	0.0162 (4)
C5	0.0492 (6)	0.07747 (18)	0.15754 (9)	0.0125 (6)
C4	0.0441 (6)	0.16715 (18)	0.12052 (9)	0.0129 (5)
C2	0.3969 (6)	0.25329 (19)	0.18127 (10)	0.0141 (6)
H2	0.5140	0.3108	0.1891	0.017*
C6	0.2263 (6)	0.07808 (18)	0.20552 (9)	0.0129 (6)
C3	0.2219 (6)	0.25382 (18)	0.13284 (9)	0.0134 (6)

C8	−0.3187 (6)	0.06946 (19)	0.05919 (9)	0.0148 (6)
C21	0.7270 (6)	0.24990 (19)	0.28100 (10)	0.0180 (6)
H21A	0.8237	0.2360	0.3165	0.027*
H21B	0.6110	0.3120	0.2850	0.027*
H21C	0.8653	0.2608	0.2512	0.027*
C9	−0.3109 (6)	−0.01717 (18)	0.09232 (9)	0.0135 (6)
C1	0.3956 (6)	0.16712 (19)	0.21750 (9)	0.0130 (6)
C7	−0.1488 (6)	0.16625 (19)	0.07100 (9)	0.0141 (6)
C20	0.4222 (6)	0.41995 (19)	0.10271 (10)	0.0196 (6)
H20A	0.3889	0.4738	0.0745	0.029*
H20B	0.6093	0.3906	0.0973	0.029*
H20C	0.4089	0.4502	0.1403	0.029*
C10	−0.1373 (6)	−0.01652 (19)	0.14485 (9)	0.0134 (6)
C14	−0.2956 (7)	−0.2026 (2)	0.05618 (11)	0.0214 (7)
H14	−0.2007	−0.1904	0.0218	0.026*
C22	0.0511 (6)	−0.00647 (18)	0.28793 (9)	0.0175 (6)
H22A	0.0825	−0.0669	0.3120	0.026*
H22B	−0.1383	−0.0095	0.2722	0.026*
H22C	0.0719	0.0568	0.3102	0.026*
C15	−0.2583 (7)	−0.2953 (2)	0.08090 (11)	0.0288 (8)
H15A	−0.3497	−0.3104	0.1153	0.035*
H15B	−0.1405	−0.3455	0.0639	0.035*
C13	−0.4799 (6)	−0.11548 (17)	0.07933 (10)	0.0155 (6)
H13A	−0.5731	−0.1396	0.1141	0.019*
H13B	−0.6273	−0.0988	0.0516	0.019*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O16	0.0252 (12)	0.0179 (9)	0.0146 (8)	−0.0020 (10)	−0.0054 (9)	0.0036 (7)
O11	0.0207 (11)	0.0155 (9)	0.0185 (8)	−0.0029 (9)	−0.0019 (8)	0.0038 (7)
O17	0.0168 (10)	0.0133 (8)	0.0148 (8)	0.0008 (9)	0.0016 (9)	0.0044 (7)
O19	0.0200 (11)	0.0132 (8)	0.0190 (9)	−0.0049 (9)	−0.0026 (9)	0.0042 (7)
O12	0.0164 (10)	0.0170 (9)	0.0157 (8)	−0.0003 (9)	0.0003 (9)	0.0024 (7)
O18	0.0178 (10)	0.0136 (8)	0.0171 (8)	−0.0029 (9)	−0.0039 (9)	0.0014 (7)
C5	0.0116 (15)	0.0122 (11)	0.0136 (11)	0.0032 (12)	0.0041 (12)	−0.0012 (9)
C4	0.0125 (14)	0.0135 (11)	0.0127 (11)	−0.0004 (12)	0.0021 (12)	0.0010 (9)
C2	0.0120 (15)	0.0130 (12)	0.0172 (12)	−0.0016 (12)	0.0018 (12)	−0.0018 (10)
C6	0.0130 (15)	0.0137 (12)	0.0121 (11)	0.0032 (13)	0.0011 (12)	0.0010 (9)
C3	0.0133 (15)	0.0118 (12)	0.0149 (11)	0.0030 (13)	0.0032 (13)	0.0023 (9)
C8	0.0130 (15)	0.0191 (13)	0.0122 (11)	0.0008 (13)	0.0000 (12)	−0.0005 (10)
C21	0.0190 (17)	0.0171 (13)	0.0179 (12)	−0.0043 (14)	−0.0045 (14)	−0.0024 (10)
C9	0.0118 (15)	0.0152 (12)	0.0136 (11)	−0.0009 (12)	−0.0013 (12)	−0.0013 (10)
C1	0.0102 (15)	0.0166 (12)	0.0120 (11)	0.0051 (12)	0.0004 (11)	−0.0014 (10)
C7	0.0135 (15)	0.0149 (12)	0.0140 (11)	0.0009 (13)	0.0056 (12)	0.0011 (10)
C20	0.0220 (17)	0.0168 (13)	0.0198 (12)	−0.0052 (13)	0.0005 (13)	−0.0011 (11)
C10	0.0118 (15)	0.0139 (12)	0.0144 (11)	0.0033 (11)	0.0039 (12)	0.0001 (10)
C14	0.0233 (18)	0.0216 (14)	0.0193 (12)	−0.0058 (14)	−0.0010 (14)	−0.0031 (10)

C22	0.0211 (15)	0.0171 (13)	0.0142 (11)	−0.0003 (13)	0.0024 (13)	0.0034 (10)
C15	0.036 (2)	0.0226 (15)	0.0275 (14)	0.0036 (16)	0.0000 (17)	−0.0033 (12)
C13	0.0155 (16)	0.0153 (12)	0.0156 (11)	−0.0041 (12)	−0.0031 (14)	0.0027 (10)

Geometric parameters (Å, º)

O16—C8	1.346 (3)	C8—C7	1.486 (3)
O16—H16	0.8200	C21—H21A	0.9600
O11—C10	1.226 (3)	C21—H21B	0.9600
O17—C6	1.375 (3)	C21—H21C	0.9600
O17—C22	1.436 (3)	C9—C10	1.471 (3)
O19—C3	1.361 (3)	C9—C13	1.505 (3)
O19—C20	1.439 (3)	C20—H20A	0.9600
O12—C7	1.237 (3)	C20—H20B	0.9600
O18—C1	1.350 (3)	C20—H20C	0.9600
O18—C21	1.443 (3)	C14—C15	1.318 (4)
C5—C6	1.394 (3)	C14—C13	1.501 (4)
C5—C4	1.427 (3)	C14—H14	0.9300
C5—C10	1.505 (3)	C22—H22A	0.9600
C4—C3	1.407 (3)	C22—H22B	0.9600
C4—C7	1.467 (3)	C22—H22C	0.9600
C2—C1	1.380 (3)	C15—H15A	0.9300
C2—C3	1.396 (3)	C15—H15B	0.9300
C2—H2	0.9300	C13—H13A	0.9700
C6—C1	1.406 (3)	C13—H13B	0.9700
C8—C9	1.342 (3)		
C8—O16—H16	109.5	O18—C1—C6	114.9 (2)
C6—O17—C22	113.32 (18)	C2—C1—C6	120.9 (2)
C3—O19—C20	118.60 (19)	O12—C7—C4	124.8 (2)
C1—O18—C21	117.46 (18)	O12—C7—C8	116.3 (2)
C6—C5—C4	119.5 (2)	C4—C7—C8	118.8 (2)
C6—C5—C10	120.5 (2)	O19—C20—H20A	109.5
C4—C5—C10	120.0 (2)	O19—C20—H20B	109.5
C3—C4—C5	119.1 (2)	H20A—C20—H20B	109.5
C3—C4—C7	122.1 (2)	O19—C20—H20C	109.5
C5—C4—C7	118.8 (2)	H20A—C20—H20C	109.5
C1—C2—C3	119.8 (2)	H20B—C20—H20C	109.5
C1—C2—H2	120.1	O11—C10—C9	119.1 (2)
C3—C2—H2	120.1	O11—C10—C5	121.6 (2)
O17—C6—C5	123.8 (2)	C9—C10—C5	119.3 (2)
O17—C6—C1	116.2 (2)	C15—C14—C13	124.9 (3)
C5—C6—C1	120.0 (2)	C15—C14—H14	117.5
O19—C3—C2	121.9 (2)	C13—C14—H14	117.5
O19—C3—C4	117.5 (2)	O17—C22—H22A	109.5
C2—C3—C4	120.6 (2)	O17—C22—H22B	109.5
C9—C8—O16	121.2 (2)	H22A—C22—H22B	109.5
C9—C8—C7	123.5 (2)	O17—C22—H22C	109.5

O16—C8—C7	115.26 (19)	H22A—C22—H22C	109.5
O18—C21—H21A	109.5	H22B—C22—H22C	109.5
O18—C21—H21B	109.5	C14—C15—H15A	120.0
H21A—C21—H21B	109.5	C14—C15—H15B	120.0
O18—C21—H21C	109.5	H15A—C15—H15B	120.0
H21A—C21—H21C	109.5	C14—C13—C9	112.2 (2)
H21B—C21—H21C	109.5	C14—C13—H13A	109.2
C8—C9—C10	119.4 (2)	C9—C13—H13A	109.2
C8—C9—C13	123.0 (2)	C14—C13—H13B	109.2
C10—C9—C13	117.6 (2)	C9—C13—H13B	109.2
O18—C1—C2	124.2 (2)	H13A—C13—H13B	107.9

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O16—H16···O12	0.82	2.14	2.612 (2)	117
O16—H16···O12^{i}	0.82	2.05	2.777 (2)	148
O16—H16···O19^{i}	0.82	2.40	2.926 (2)	122

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