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6,11-Dihydroxynaphthacene-5,12-dione

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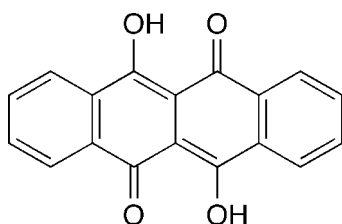
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.114; wR factor = 0.354; data-to-parameter ratio = 13.0.

The molecule of the title compound, $\text{C}_{18}\text{H}_{10}\text{O}_4$, is centrosymmetric and planar. A long phenolic O—H bond is observed [1.19 (9) Å], which is involved in an intramolecular hydrogen bond between the phenolic and quinonoid O atoms. The molecules pack in a herringbone pattern and are linked to each other *via* intermolecular C—H $\cdots$ O hydrogen bonds (2.73–2.77 Å).

Related literature

The crystal structure of the rhenium complex including the title compound has been reported (Sathiyendiran *et al.*, 2007). For studies of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone), see: Fehlmann & Nigli (1965); Cradwick & Hall (1971); Herbstein *et al.* (1985); Rubio *et al.* (1985); Sarkhel *et al.* (2001); Savko *et al.* (2007). For background on intramolecular hydrogen bonds, see: Gilli *et al.* (1989); Bertolasi *et al.* (1991); Gilli *et al.* (1993); Steiner & Saenger (1994). For background on intermolecular hydrogen bonds, see: Taylor & Kennard (1982); Jagarlapudi & Desiraju (1987); Biradha *et al.* (1993); Batchelor *et al.* (2000). For background on resonance structures, see: Cradwick & Hall (1971); Shiao *et al.* (1980).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{10}\text{O}_4$
 $M_r = 290.26$
 Monoclinic, $P2_1/c$

$a = 8.85$ (2) Å
 $b = 3.750$ (8) Å
 $c = 18.74$ (4) Å

$\beta = 94.55$ (3)°
 $V = 620$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.11$ mm⁻¹
 $T = 173$ (2) K
 $0.29 \times 0.07 \times 0.03$ mm

Data collection

Rigaku Mercury CCD
 diffractometer
 Absorption correction: none
 5026 measured reflections

1347 independent reflections
 668 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.114$
 $wR(F^2) = 0.354$
 $S = 0.99$
 1347 reflections
 104 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}$	1.19 (9)	1.56 (9)	2.516 (7)	132 (6)
$\text{C6}-\text{H6}\cdots\text{O1}^{\text{i}}$	0.95	2.77	3.449 (9)	129
$\text{C6}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.95	2.74	3.382 (9)	126
$\text{C3}-\text{H3}\cdots\text{O2}^{\text{iii}}$	0.95	2.75	3.378 (10)	124
$\text{C4}-\text{H4}\cdots\text{O2}^{\text{iii}}$	0.95	2.73	3.371 (9)	126

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

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2022).

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supporting information

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6,11-Dihydroxynaphthacene-5,12-dione

Masaaki Tomura, Hiroyuki Yamaguchi, Katsuhiko Ono and Katsuhiro Saito

S1. Comment

Organic molecules containing naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) skeleton have been the attractive subject of structural investigations (Fehlmann & Nigli, 1965; Cradwick & Hall, 1971; Herbstein *et al.*, 1985; Rubio *et al.*, 1985; Sarkhel *et al.*, 2001; Savko *et al.*, 2007). The title compound, (I) (Fig. 1), is π -extended naphthazarin and its molecular and crystal structures are described here.

The molecule of (I) is centrosymmetric and planar, with an r.m.s deviation of 0.0098 Å from the least-squares plane for the fitted non-H atoms. The molecular structure is similar to that of naphthazarin. The symmetry of the carbon skeleton of (I) is close to D_{2h} (Table 1). The long phenolic O2—H2 bond [1.19 (9) Å] constitutes an intramolecular hydrogen bond between the phenolic O2 and quinonoid O1 atoms (Gilli *et al.*, 1989; Bertolasi *et al.*, 1991; Gilli *et al.*, 1993; Steiner & Saenger, 1994). These facts imply that the structure of (I) can be interpreted not as 1,4- nor 1,5-quinone but as resonance between two zwitterion contributors, as shown in Scheme 1 (Cradwick & Hall, 1971; Shiau *et al.*, 1980).

In the crystal structure, the molecules form a herringbone-type stacking along the *b* axis, where the distance between the molecular planes is 3.42 Å (Fig. 2). The packing mode is similar to that characteristic of aromatic hydrocarbon atoms. The intermolecular C—H $\cdots$ O hydrogen bonds (Taylor & Kennard, 1982; Jagarlapudi & Desiraju, 1987; Biradha *et al.*, 1993; Batchelor *et al.*, 2000) are found between the herringbone-type stackings (Table 2). Similar C—H $\cdots$ O hydrogen bonds (2.54–3.01 Å) were observed in the crystal structure of naphthazarin (Cradwick & Hall, 1971).

S2. Experimental

The title compound (I) was commercially available. Red crystals of (I) suitable for X-ray analysis were grown from a chloroform solution.

S3. Refinement

The H atom bonded to the phenolic O atom was located in a difference map and refined isotropically. Other H atoms were positioned geometrically refined using a riding model with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

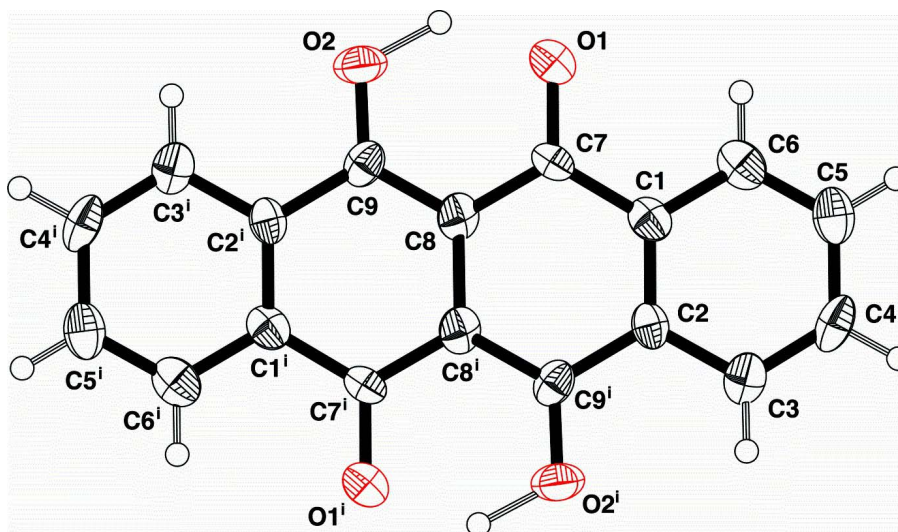


Figure 1

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $-x, -y, -z + 1$].

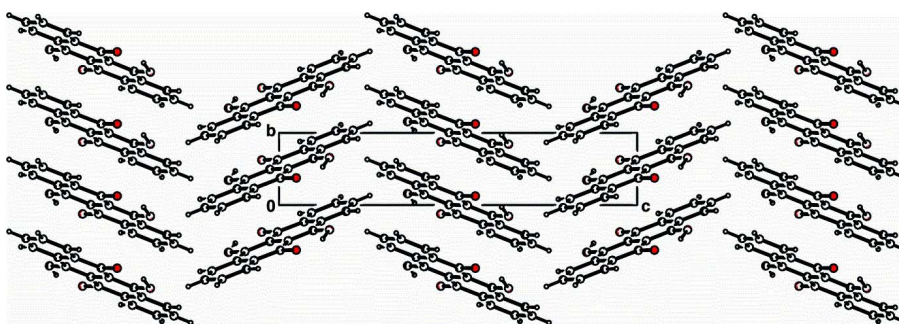


Figure 2

The packing diagram of (I), viewed along the a axis.

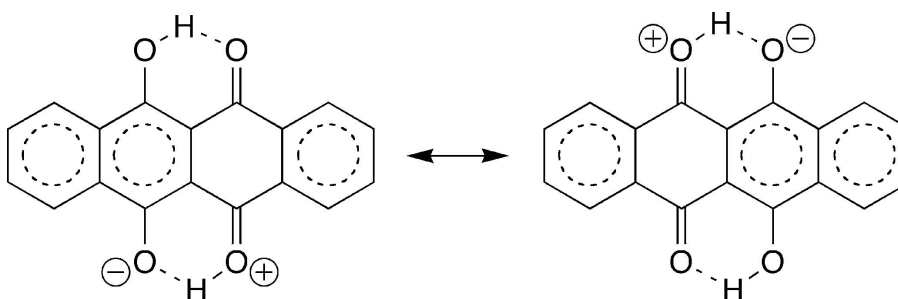


Figure 3

The resonance structure of (I).

6,11-Dihydroxynaphthacene-5,12-dione

Crystal data

$C_{18}H_{10}O_4$
 $M_r = 290.26$

Monoclinic, $P2_1/c$
Hall symbol: $-P\ 2_1bc$

$a = 8.85$ (2) Å
 $b = 3.750$ (8) Å
 $c = 18.74$ (4) Å
 $\beta = 94.55$ (3)°
 $V = 620$ (2) Å³
 $Z = 2$
 $F(000) = 300$
 $D_x = 1.555$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
 Cell parameters from 928 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 0.11$ mm⁻¹
 $T = 173$ K
 Prism, red
 $0.29 \times 0.07 \times 0.03$ mm

Data collection

Rigaku Mercury CCD
 diffractometer
 Radiation source: Rotating Anode
 Graphite Monochromator monochromator
 Detector resolution: 14.6199 pixels mm⁻¹
 φ and ω scans
 5026 measured reflections

1347 independent reflections
 668 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.1^\circ$
 $h = -9 \rightarrow 11$
 $k = -4 \rightarrow 3$
 $l = -19 \rightarrow 24$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.114$
 $wR(F^2) = 0.354$
 $S = 0.99$
 1347 reflections
 104 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
 $w = 1/[\sigma^2(F_o^2) + (0.1532P)^2 + 1.2875P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.053$
 $\Delta\rho_{\text{max}} = 0.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.3137 (5)	0.1246 (12)	0.4518 (2)	0.0438 (12)
O2	0.1298 (5)	-0.1563 (12)	0.3591 (2)	0.0426 (12)
H2	0.248 (10)	-0.03 (3)	0.378 (5)	0.09 (3)*
C1	0.2384 (6)	0.2682 (14)	0.5696 (3)	0.0317 (13)
C2	0.1249 (6)	0.2760 (13)	0.6171 (3)	0.0290 (12)
C3	0.1583 (7)	0.4134 (15)	0.6871 (3)	0.0363 (14)
H3	0.0823	0.4198	0.7201	0.044*
C4	0.3022 (7)	0.5375 (15)	0.7068 (3)	0.0381 (15)
H4	0.3247	0.6318	0.7535	0.046*

C5	0.4162 (7)	0.5264 (15)	0.6586 (3)	0.0403 (15)
H5	0.5151	0.6117	0.6728	0.048*
C6	0.3839 (7)	0.3917 (14)	0.5910 (3)	0.0371 (14)
H6	0.4611	0.3823	0.5586	0.045*
C7	0.2079 (6)	0.1277 (14)	0.4965 (3)	0.0294 (12)
C8	0.0599 (6)	−0.0051 (14)	0.4744 (3)	0.0312 (13)
C9	0.0278 (7)	−0.1452 (13)	0.4050 (3)	0.0308 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.034 (2)	0.052 (3)	0.046 (3)	−0.011 (2)	0.0070 (18)	−0.004 (2)
O2	0.042 (3)	0.048 (3)	0.041 (2)	0.000 (2)	0.0186 (19)	−0.0051 (19)
C1	0.027 (3)	0.025 (3)	0.043 (3)	0.003 (2)	0.002 (2)	−0.001 (2)
C2	0.028 (3)	0.024 (3)	0.034 (3)	0.000 (2)	−0.005 (2)	0.001 (2)
C3	0.049 (4)	0.028 (3)	0.031 (3)	−0.005 (3)	−0.003 (2)	0.004 (2)
C4	0.063 (4)	0.027 (3)	0.023 (3)	−0.001 (3)	−0.008 (3)	0.000 (2)
C5	0.042 (3)	0.031 (3)	0.045 (3)	−0.001 (3)	−0.011 (3)	0.002 (3)
C6	0.038 (3)	0.022 (3)	0.052 (4)	−0.004 (2)	0.004 (3)	0.005 (2)
C7	0.021 (3)	0.030 (3)	0.037 (3)	−0.001 (2)	0.005 (2)	0.002 (2)
C8	0.036 (3)	0.031 (3)	0.025 (3)	0.001 (2)	−0.006 (2)	0.012 (2)
C9	0.044 (3)	0.021 (2)	0.028 (3)	−0.002 (2)	0.002 (2)	−0.002 (2)

Geometric parameters (Å, °)

O1—C7	1.304 (6)	C4—C5	1.407 (9)
O2—C9	1.296 (7)	C4—H4	0.9500
O2—H2	1.19 (9)	C5—C6	1.373 (8)
C1—C2	1.395 (8)	C5—H5	0.9500
C1—C6	1.398 (8)	C6—H6	0.9500
C1—C7	1.472 (8)	C7—C8	1.432 (8)
C2—C3	1.418 (8)	C8—C9	1.410 (7)
C2—C9 ⁱ	1.467 (8)	C8—C8 ⁱ	1.486 (11)
C3—C4	1.378 (9)	C9—C2 ⁱ	1.467 (8)
C3—H3	0.9500		
C7—O1—H2	110 (3)	C6—C5—H5	120.1
C9—O2—H2	115 (4)	C4—C5—H5	120.1
C2—C1—C6	120.2 (5)	C5—C6—C1	120.4 (6)
C2—C1—C7	120.9 (5)	C5—C6—H6	119.8
C6—C1—C7	118.9 (5)	C1—C6—H6	119.8
C1—C2—C3	119.4 (5)	O1—C7—C8	119.9 (5)
C1—C2—C9 ⁱ	120.4 (5)	O1—C7—C1	120.8 (5)
C3—C2—C9 ⁱ	120.2 (5)	C8—C7—C1	119.3 (5)
C2—C3—C4	119.4 (5)	C9—C8—C7	120.6 (5)
C2—C3—H3	120.3	C9—C8—C8 ⁱ	120.2 (6)
C4—C3—H3	120.3	C7—C8—C8 ⁱ	119.2 (6)
C3—C4—C5	120.8 (5)	O2—C9—C8	121.6 (5)

C3—C4—H4	119.6	O2—C9—C2 ⁱ	118.4 (5)
C5—C4—H4	119.6	C8—C9—C2 ⁱ	119.9 (5)
C6—C5—C4	119.7 (6)		
C6—C1—C2—C3	0.6 (8)	C6—C1—C7—O1	−1.4 (8)
C7—C1—C2—C3	−180.0 (5)	C2—C1—C7—C8	−0.5 (8)
C6—C1—C2—C9 ⁱ	−179.7 (5)	C6—C1—C7—C8	178.9 (5)
C7—C1—C2—C9 ⁱ	−0.3 (8)	O1—C7—C8—C9	1.1 (7)
C1—C2—C3—C4	0.2 (7)	C1—C7—C8—C9	−179.3 (5)
C9 ⁱ —C2—C3—C4	−179.5 (5)	O1—C7—C8—C8 ⁱ	−179.1 (6)
C2—C3—C4—C5	−0.6 (8)	C1—C7—C8—C8 ⁱ	0.6 (8)
C3—C4—C5—C6	0.3 (8)	C7—C8—C9—O2	−0.5 (8)
C4—C5—C6—C1	0.5 (8)	C8 ⁱ —C8—C9—O2	179.7 (6)
C2—C1—C6—C5	−0.9 (8)	C7—C8—C9—C2 ⁱ	−179.2 (5)
C7—C1—C6—C5	179.6 (5)	C8 ⁱ —C8—C9—C2 ⁱ	1.0 (8)
C2—C1—C7—O1	179.2 (5)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ O1	1.19 (9)	1.56 (9)	2.516 (7)	132 (6)
C6—H6 $\cdots$ O1 ⁱⁱ	0.95	2.77	3.449 (9)	129
C6—H6 $\cdots$ O1 ⁱⁱⁱ	0.95	2.74	3.382 (9)	126
C3—H3 $\cdots$ O2 ^{iv}	0.95	2.75	3.378 (10)	124
C4—H4 $\cdots$ O2 ^{iv}	0.95	2.73	3.371 (9)	126

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