

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-Hydroxy-1-methoxyanthraquinone monohydrate

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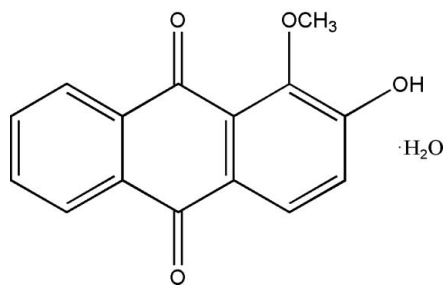
Received 4 May 2009; accepted 4 June 2009

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.046; wR factor = 0.147; data-to-parameter ratio = 11.5.

The title compound, $\text{C}_{15}\text{H}_{10}\text{O}_4 \cdot \text{H}_2\text{O}$, also known as alizarin 1-methyl ether monohydrate, was isolated from *Morinda officinalis* How. The anthraquinone ring system is almost planar, the dihedral angle between the two outer benzene rings being 3.07 (4)°. In the crystal structure, $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds link the organic molecules and the water molecules, forming a three-dimensional network.

Related literature

For pharmacological properties of anthraquinone derivatives, see: Kim *et al.* (2005) and of 1-methoxy-2-hydroxyanthraquinone, see: Ali *et al.* (2000); Jia *et al.* (2007); Wu *et al.* (2003). For related structures, see: Boonnak *et al.* (2005); Ng *et al.* (2005). For the structure of another compound isolated from *Morinda officinalis* How., see: Xu *et al.* (2009). For reference structural data, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{15}\text{H}_{10}\text{O}_4 \cdot \text{H}_2\text{O}$
 $M_r = 272.25$

 Triclinic, $P\bar{1}$
 $a = 7.9583$ (19) Å

 $b = 8.269$ (2) Å

 $c = 10.188$ (2) Å

 $\alpha = 102.462$ (3)°

 $\beta = 102.364$ (3)°

 $\gamma = 100.653$ (3)°

 $V = 620.4$ (2) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 0.11$ mm⁻¹
 $T = 298$ K

 $0.30 \times 0.20 \times 0.15$ mm

Data collection

Bruker APEXII area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\min} = 0.973$, $T_{\max} = 0.986$

3218 measured reflections

2198 independent reflections

 1488 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.147$
 $S = 1.04$

2198 reflections

191 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1W}-\text{H1W} \cdots \text{O2}^i$	0.86 (3)	2.31 (2)	2.960 (3)	133 (3)
$\text{O1W}-\text{H2W} \cdots \text{O4}^{ii}$	0.87 (3)	2.30 (2)	3.072 (3)	149 (3)
$\text{O3}-\text{H3} \cdots \text{O1W}$	0.82	1.87	2.687 (2)	173

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

The authors acknowledge South China University of Technology and Dongguan University of Technology for support of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2258).

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supplementary materials

Acta Cryst. (2009). E65, o1523 [doi:10.1107/S1600536809021254]

2-Hydroxy-1-methoxyanthraquinone monohydrate

Z.-M. Liu and Y.-Q. Jiao

Comment

Anthraquinone derivatives extracted from the roots of *Morinda officinalis* How (most common familiar name in China: Bajitian) have been used in China since ancient times to treat a wide range of symptoms including poor digestion, high blood pressure and immune deficiencies. Recent studies have demonstrated that they have multiple pharmacological actions (Kim *et al.*, 2005). One component found in *Morinda officinalis* How, 1-Methoxy-2-hydroxyanthraquinone, is known as alizarin-1-methylether and exhibits a variety of potent biological effects such as antiviral and antimicrobial activities (Ali *et al.*, 2000), antioxidant activity (Jia *et al.*, 2007) and cytotoxic activity (Wu *et al.*, 2003). We report here the structure of the monohydrate.

In the title compound (Fig. 1), the C-C bond lengths show normal values (Allen *et al.*, 1987), and the C-O and C=O bond lengths are comparable to those observed in similar structures (Ng *et al.*, 2005; Boonnak *et al.*, 2005). The anthraquinone ring system is substantially planar, the dihedral angle between the two benzene rings being $3.07(4)^\circ$. In the crystal structure, the crystal water connects with alizarin-1-methylether by O—H \cdots O hydrogen bonds. The molecules are self-assembled by O—H \cdots O hydrogen bonding interactions (Table 1 and Fig. 2) into a supramolecular network.

Experimental

The roots of *Morinda officinalis* How (1000 g) were shattered to powder (about 30 mesh) and extracted with 85% ethanol (4000 ml) for 2 h with stirring. The extraction procedure was repeated three times. The extracts were combined and evaporated to dryness under reduced pressure at 333 K, the residue was redissolved in water (800 ml). Then the enriched extracts were extracted with chloroform three times (800 ml for each time), the chloroform solution were combined and evaporated to dryness under reduced pressure at 333 K. 6.80 g of crude extracts were obtained. The crude extracts were separated with n-hexane-ethyl acetate-methanol-water (6 : 4 : 5 : 5, v/v) using high-speed counter-current chromatography (HSCCC) to obtain 1-Methoxy-2-hydroxyanthraquinone (yield 90.6 mg). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

Refinement

H atoms not pertaining to water molecules were placed at calculated positions and treated as riding on the parent atoms with C—H = 0.93–0.97 and O—H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C}, \text{O})$. The water hydrogen atoms were found from the Fourier maps and refined with restrained O-H=0.86 (3)Å and free $U_{\text{iso}}(\text{H})$.

Figures

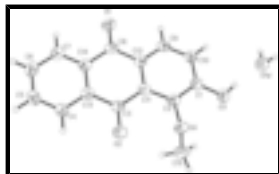


Fig. 1. The molecular structure showing the atomic-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

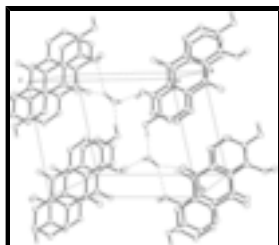


Fig. 2. The molecular packing showing the hydrogen bonding interactions as broken lines.

2-Hydroxy-1-methoxyanthraquinone monohydrate

Crystal data

$C_{15}H_{10}O_4 \cdot H_2O$

$M_r = 272.25$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.9583$ (19) Å

$b = 8.269$ (2) Å

$c = 10.188$ (2) Å

$\alpha = 102.462$ (3)°

$\beta = 102.364$ (3)°

$\gamma = 100.653$ (3)°

$V = 620.4$ (2) Å³

$Z = 2$

$F_{000} = 284.0$

$D_x = 1.457$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1018 reflections

$\theta = 2.6$ – 26.2 °

$\mu = 0.11$ mm⁻¹

$T = 298$ K

Block, yellow

$0.30 \times 0.20 \times 0.15$ mm

Data collection

Bruker APEXII area-detector diffractometer

2198 independent reflections

Radiation source: fine-focus sealed tube

1488 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$R_{int} = 0.013$

$T = 298$ K

$\theta_{max} = 25.2$ °

ϕ and ω scans

$\theta_{min} = 2.1$ °

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$h = -9 \rightarrow 9$

$T_{min} = 0.973$, $T_{max} = 0.986$

$k = -9 \rightarrow 9$

3218 measured reflections

$l = -12 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.147$	$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.0805P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2198 reflections	$(\Delta/\sigma)_{\max} < 0.001$
191 parameters	$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6640 (3)	0.3815 (2)	0.3121 (2)	0.0509 (5)
C2	0.7049 (3)	0.2214 (2)	0.30375 (19)	0.0476 (5)
C3	0.7720 (3)	-0.0406 (2)	0.1655 (2)	0.0485 (5)
C4	0.8497 (3)	-0.2806 (2)	0.0176 (2)	0.0555 (5)
H4	0.8772	-0.3219	0.0955	0.067*
C5	0.8632 (3)	-0.3695 (3)	-0.1086 (3)	0.0645 (6)
H5	0.8980	-0.4717	-0.1158	0.077*
C6	0.8257 (3)	-0.3093 (3)	-0.2248 (3)	0.0668 (6)
H6	0.8347	-0.3707	-0.3099	0.080*
C7	0.7746 (3)	-0.1565 (3)	-0.2142 (2)	0.0600 (6)
H7	0.7505	-0.1146	-0.2921	0.072*
C8	0.7044 (3)	0.0971 (2)	-0.07708 (19)	0.0500 (5)
C9	0.6444 (3)	0.3450 (2)	0.0710 (2)	0.0514 (5)
H9	0.6210	0.3853	-0.0078	0.062*
C10	0.6335 (3)	0.4407 (3)	0.1954 (2)	0.0542 (5)
H10	0.6054	0.5458	0.2006	0.065*

supplementary materials

C11	0.7216 (2)	0.1254 (2)	0.17820 (19)	0.0438 (5)
C12	0.6896 (2)	0.1890 (2)	0.06001 (19)	0.0444 (5)
C13	0.7951 (2)	-0.1285 (2)	0.0293 (2)	0.0462 (5)
C14	0.7593 (2)	-0.0664 (2)	-0.08792 (19)	0.0472 (5)
C15	0.8905 (4)	0.2159 (3)	0.5181 (2)	0.0869 (8)
H15A	0.9726	0.1661	0.4763	0.130*
H15B	0.8843	0.1791	0.6005	0.130*
H15C	0.9298	0.3380	0.5425	0.130*
O1	0.6741 (2)	0.15409 (19)	-0.17812 (15)	0.0741 (5)
O2	0.7941 (3)	-0.10671 (19)	0.26171 (16)	0.0772 (5)
O3	0.6543 (2)	0.46790 (18)	0.43714 (14)	0.0679 (5)
H3	0.6315	0.5594	0.4317	0.102*
O4	0.7180 (2)	0.16259 (18)	0.42088 (14)	0.0616 (4)
O1W	0.5800 (3)	0.7728 (2)	0.44181 (19)	0.0829 (6)
H1W	0.597 (4)	0.844 (4)	0.393 (4)	0.162 (15)*
H2W	0.472 (2)	0.762 (4)	0.450 (4)	0.134 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0497 (12)	0.0517 (11)	0.0508 (11)	0.0118 (9)	0.0133 (9)	0.0132 (9)
C2	0.0446 (11)	0.0537 (11)	0.0457 (11)	0.0084 (9)	0.0097 (8)	0.0211 (9)
C3	0.0464 (11)	0.0500 (11)	0.0492 (11)	0.0071 (9)	0.0100 (9)	0.0196 (9)
C4	0.0493 (12)	0.0548 (12)	0.0635 (13)	0.0132 (9)	0.0144 (10)	0.0182 (10)
C5	0.0549 (14)	0.0588 (13)	0.0799 (16)	0.0187 (10)	0.0190 (11)	0.0134 (11)
C6	0.0577 (14)	0.0715 (15)	0.0633 (14)	0.0117 (12)	0.0181 (11)	0.0030 (11)
C7	0.0561 (13)	0.0671 (14)	0.0510 (12)	0.0073 (11)	0.0120 (10)	0.0128 (10)
C8	0.0450 (11)	0.0557 (11)	0.0432 (11)	0.0020 (9)	0.0041 (8)	0.0166 (9)
C9	0.0515 (12)	0.0506 (11)	0.0516 (11)	0.0082 (9)	0.0067 (9)	0.0226 (9)
C10	0.0557 (13)	0.0504 (11)	0.0565 (12)	0.0133 (9)	0.0096 (10)	0.0191 (10)
C11	0.0370 (10)	0.0449 (10)	0.0490 (11)	0.0051 (8)	0.0090 (8)	0.0179 (8)
C12	0.0384 (10)	0.0451 (10)	0.0462 (11)	0.0028 (8)	0.0060 (8)	0.0163 (8)
C13	0.0360 (10)	0.0464 (11)	0.0533 (11)	0.0039 (8)	0.0094 (8)	0.0146 (9)
C14	0.0382 (10)	0.0504 (11)	0.0468 (11)	0.0010 (8)	0.0082 (8)	0.0115 (8)
C15	0.100 (2)	0.0976 (19)	0.0591 (15)	0.0295 (16)	-0.0015 (14)	0.0303 (14)
O1	0.1049 (13)	0.0732 (10)	0.0481 (9)	0.0260 (9)	0.0141 (8)	0.0263 (7)
O2	0.1226 (15)	0.0696 (10)	0.0615 (10)	0.0433 (10)	0.0352 (9)	0.0355 (8)
O3	0.0926 (12)	0.0649 (10)	0.0561 (9)	0.0349 (9)	0.0257 (8)	0.0172 (7)
O4	0.0760 (10)	0.0684 (9)	0.0503 (8)	0.0229 (8)	0.0207 (7)	0.0277 (7)
O1W	0.1221 (18)	0.0768 (12)	0.0776 (12)	0.0454 (11)	0.0478 (11)	0.0384 (10)

Geometric parameters (\AA , $^\circ$)

C1—O3	1.345 (2)	C8—O1	1.218 (2)
C1—C10	1.373 (3)	C8—C12	1.479 (3)
C1—C2	1.410 (3)	C8—C14	1.486 (3)
C2—O4	1.374 (2)	C9—C10	1.371 (3)
C2—C11	1.399 (3)	C9—C12	1.390 (3)
C3—O2	1.218 (2)	C9—H9	0.9300

C3—C13	1.487 (3)	C10—H10	0.9300
C3—C11	1.487 (3)	C11—C12	1.408 (2)
C4—C5	1.373 (3)	C13—C14	1.395 (3)
C4—C13	1.394 (3)	C15—O4	1.437 (3)
C4—H4	0.9300	C15—H15A	0.9600
C5—C6	1.377 (3)	C15—H15B	0.9600
C5—H5	0.9300	C15—H15C	0.9600
C6—C7	1.387 (3)	O3—H3	0.8200
C6—H6	0.9300	O1W—H1W	0.86 (3)
C7—C14	1.382 (3)	O1W—H2W	0.87 (3)
C7—H7	0.9300		
O3—C1—C10	123.24 (18)	C12—C9—H9	119.2
O3—C1—C2	116.77 (17)	C9—C10—C1	120.01 (18)
C10—C1—C2	119.98 (18)	C9—C10—H10	120.0
O4—C2—C11	122.55 (17)	C1—C10—H10	120.0
O4—C2—C1	117.08 (17)	C2—C11—C12	118.56 (17)
C11—C2—C1	120.29 (16)	C2—C11—C3	122.38 (16)
O2—C3—C13	119.21 (18)	C12—C11—C3	119.06 (17)
O2—C3—C11	122.56 (18)	C9—C12—C11	119.58 (18)
C13—C3—C11	118.22 (16)	C9—C12—C8	117.85 (17)
C5—C4—C13	120.20 (19)	C11—C12—C8	122.57 (17)
C5—C4—H4	119.9	C4—C13—C14	118.95 (18)
C13—C4—H4	119.9	C4—C13—C3	118.85 (17)
C4—C5—C6	120.9 (2)	C14—C13—C3	122.18 (17)
C4—C5—H5	119.6	C7—C14—C13	120.27 (19)
C6—C5—H5	119.6	C7—C14—C8	119.88 (18)
C5—C6—C7	119.6 (2)	C13—C14—C8	119.85 (18)
C5—C6—H6	120.2	O4—C15—H15A	109.5
C7—C6—H6	120.2	O4—C15—H15B	109.5
C14—C7—C6	120.1 (2)	H15A—C15—H15B	109.5
C14—C7—H7	120.0	O4—C15—H15C	109.5
C6—C7—H7	119.9	H15A—C15—H15C	109.5
O1—C8—C12	121.26 (19)	H15B—C15—H15C	109.5
O1—C8—C14	120.74 (18)	C1—O3—H3	109.5
C12—C8—C14	117.99 (16)	C2—O4—C15	115.30 (16)
C10—C9—C12	121.52 (18)	H1W—O1W—H2W	107.3 (16)
C10—C9—H9	119.2		
O3—C1—C2—O4	4.7 (3)	C3—C11—C12—C8	-0.1 (3)
C10—C1—C2—O4	-174.23 (17)	O1—C8—C12—C9	-1.6 (3)
O3—C1—C2—C11	-178.49 (17)	C14—C8—C12—C9	177.72 (16)
C10—C1—C2—C11	2.6 (3)	O1—C8—C12—C11	179.19 (17)
C13—C4—C5—C6	1.0 (3)	C14—C8—C12—C11	-1.5 (3)
C4—C5—C6—C7	0.3 (3)	C5—C4—C13—C14	-1.7 (3)
C5—C6—C7—C14	-0.7 (3)	C5—C4—C13—C3	176.53 (17)
C12—C9—C10—C1	-1.3 (3)	O2—C3—C13—C4	-3.0 (3)
O3—C1—C10—C9	-179.48 (18)	C11—C3—C13—C4	177.29 (16)
C2—C1—C10—C9	-0.6 (3)	O2—C3—C13—C14	175.24 (18)
O4—C2—C11—C12	174.08 (16)	C11—C3—C13—C14	-4.5 (3)

supplementary materials

C1—C2—C11—C12	-2.5 (3)	C6—C7—C14—C13	-0.1 (3)
O4—C2—C11—C3	-6.0 (3)	C6—C7—C14—C8	-179.97 (18)
C1—C2—C11—C3	177.34 (16)	C4—C13—C14—C7	1.3 (3)
O2—C3—C11—C2	3.3 (3)	C3—C13—C14—C7	-176.93 (17)
C13—C3—C11—C2	-176.94 (16)	C4—C13—C14—C8	-178.80 (17)
O2—C3—C11—C12	-176.78 (18)	C3—C13—C14—C8	3.0 (3)
C13—C3—C11—C12	2.9 (3)	O1—C8—C14—C7	-0.7 (3)
C10—C9—C12—C11	1.3 (3)	C12—C8—C14—C7	179.92 (16)
C10—C9—C12—C8	-177.90 (17)	O1—C8—C14—C13	179.34 (18)
C2—C11—C12—C9	0.6 (3)	C12—C8—C14—C13	0.0 (3)
C3—C11—C12—C9	-179.25 (16)	C11—C2—O4—C15	95.3 (2)
C2—C11—C12—C8	179.82 (16)	C1—C2—O4—C15	-87.9 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W \cdots O2 ⁱ	0.86 (3)	2.31 (2)	2.960 (3)	133 (3)
O1W—H2W \cdots O4 ⁱⁱ	0.87 (3)	2.30 (2)	3.072 (3)	149 (3)
O3—H3 \cdots O1W	0.82	1.87	2.687 (2)	173

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

Fig. 1

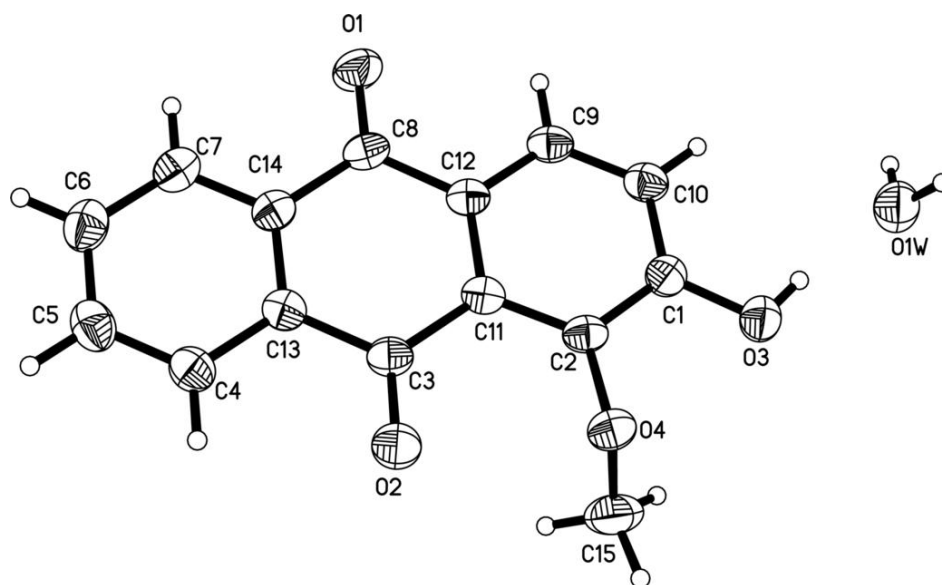


Fig. 2

