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1,8-Dihydroxyanthraquinone

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Key indicators

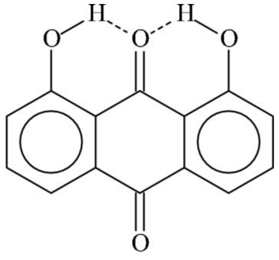
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.047
wR factor = 0.153
Data-to-parameter ratio = 9.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

1,8-Dihydroxyanthraquinone lies on a special position of site symmetry 2; a van der Waals interaction between the 9-carbonyl O atom of one molecule and the 10-carbonyl O atom of another links adjacent molecules into a linear chain [O···O = 2.779 (3) Å].

Comment

The space group of 1,8-dihydroxyanthraquinone was determined as either $P4_1$ or $P4_3$ from photographic measurements (Jagannadham, 1957); the crystal structure was later described in this tetragonal system (Prakash, 1962; 1965). A check on the atomic coordinates of the compound, listed as DHANQU in the Cambridge Structural Database [Version 5.26; Allen (2002)], with *PLATON* (Spek, 2003) did not find any higher symmetry.



(I)

Other studies have reported the existence of two forms of 1,8-dihydroxyanthraquinone; the metastable form changes to

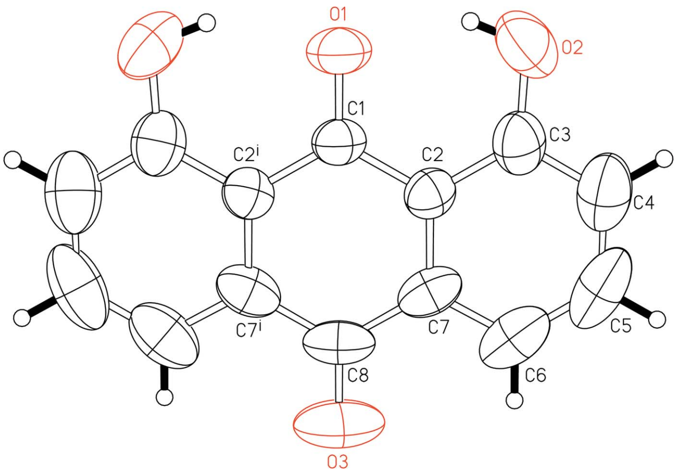


Figure 1
ORTEP (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Symmetry code (i) *y*, *x*, −*z*.

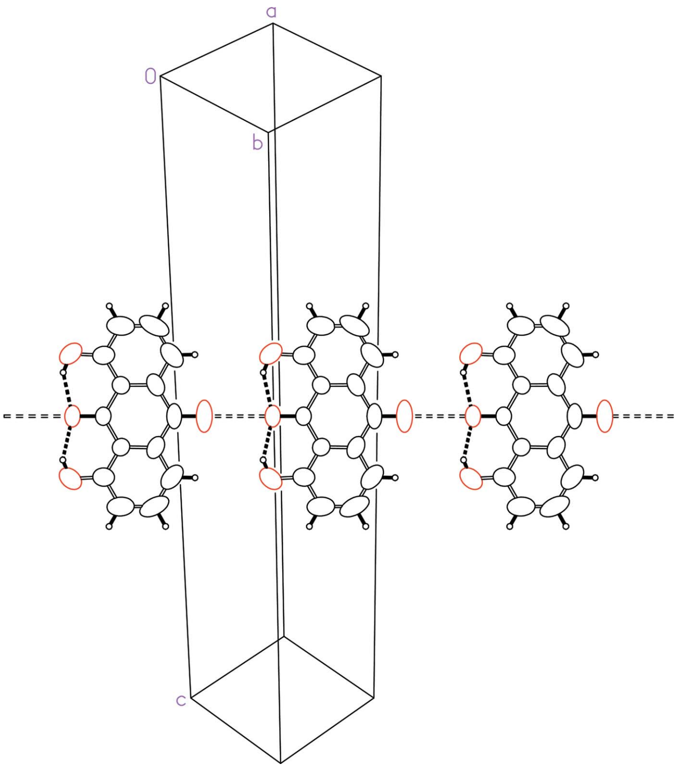


Figure 2
ORTEP (Johnson, 1976) plot of the intermolecular $O_{carbonyl}\cdots O_{carbonyl}$ interaction that links adjacent molecules into a linear chain [$O1\cdots O3^{i}$ = 2.779 (3) Å; symmetry code: (i) $1 + x$, $1 + y$, z].

the stable form as a consequence of the rotation of the intramolecular hydrogen bond. The metastable form has two equivalent intramolecular hydrogen bonds (Smulevich *et al.*, 1987; Smulevich & Marzocchi, 1985).

Recrystallization of 1,8-dihydroxyanthraquinone from pyridine has furnished a compound that crystallizes in the higher-symmetry $P4_12_12$ (or the enantiomorphous $P4_32_12$) space group. A twofold rotation axis passes through the two carbonyl groups, and the hydroxy group forms an intramolecular hydrogen bond [$O\cdots O$ = 2.535 (3) Å] (Fig. 1). Other interactions are not present in the planar molecule; however, adjacent molecules interact through the carbonyl O atoms, generating a linear chain motif (Fig. 2). The carbonyl group that is involved in hydrogen bonding has a longer C═O bond than the carbonyl group that is not involved in hydrogen bonding. This higher symmetry form may be the metastable form observed in the above-mentioned infrared study.

Geometry-optimization calculations with *HYPERCHEM* (Hypercube, 2000) at PM3 level give two minimum conformations, one with the doubly bonded O atom at the 9-position linked intramolecularly by one hydrogen bond, and the other with this atom linked intramolecularly by two hydrogen bonds. The second conformation is about 5.5 kcal mol^{-1} thermodynamically more stable, the conversion of the second form to the first requiring an energy of only about 2 kcal mol^{-} (*cf.* kT = 0.59 kcal mol^{-1}). In addition, ZINDO/S calculations show that the first allowed electronic transition is a π to π^{*} transition with a small contribution of n to π^{*} from one of the hydroxy groups. The difference of about 10 nm between the two forms may explain the slight difference in color that has been noted for the two polymorphs.

Experimental

Commerically available, reddish-brown 1,8-dihydroxyanthraquinone was recrystallized from pyridine to afford rust-red crystals.

The color is orange when the compound is recrystallized from an acetone/acetonitrile mixture; this compound belongs to $P4_1$ (or the enantiomorphous $P4_3$) space group, and it crystallizes as plates (Claborn *et al.*, 2003).

Crystal data

$C_{14}H_8O_4$
M_r = 240.20
Tetragonal, $P4_12_12$
a = 5.7440 (6) Å
c = 31.393 (3) Å
V = 1035.8 (2) $Å^3$
Z = 4
D_x = 1.540 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1561 reflections
θ = 3.6–21.9°
μ = 0.11 mm^{-1}
T = 295 (2) K
Block, red
0.37 × 0.34 × 0.28 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scan
Absorption correction: None
6173 measured reflections
766 independent reflections

509 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.0°
$h = -7 \rightarrow 7$
$k = -6 \rightarrow 7$
$l = -36 \rightarrow 39$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.153
S = 1.10
766 reflections
85 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2 + 0.1067P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.12 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.14 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.247 (4)	C3—C4	1.383 (5)
O2—C3	1.344 (4)	C4—C5	1.363 (5)
O3—C8	1.219 (5)	C5—C6	1.389 (6)
C1—C2	1.447 (3)	C6—C7	1.376 (5)
C2—C3	1.405 (4)	C7—C8	1.479 (4)
C2—C7	1.406 (4)		
O1—C1—C2	119.9 (2)	C5—C4—C3	119.9 (4)
O1—C1—C2^{i}	119.9 (2)	C4—C5—C6	121.3 (4)
C2—C1—C2^{i}	120.3 (3)	C7—C6—C5	119.9 (4)
C3—C2—C7	119.4 (3)	C6—C7—C2	119.6 (3)
C3—C2—C1	120.0 (3)	C6—C7—C8	120.6 (3)
C7—C2—C1	120.6 (3)	C2—C7—C8	119.8 (3)
O2—C3—C4	117.3 (3)	O3—C8—C7	120.6 (2)
O2—C3—C2	122.8 (3)	C7—C8—C7^{i}	118.9 (4)
C4—C3—C2	119.9 (4)		

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

Of the two possible space groups, $P4_12_12$ and $P4_32_12$, the first was chosen arbitrarily. In the absence of significantanomalous scattering effects, Friedel pairs were merged.

H atoms were placed at calculated positions (C–H 0.93 and O—H 0.82 Å) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C,O)$. The hydroxy group was rotated to fit the electron density.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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References

Allen F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bruker (2001). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2003). *SAINT*. Version 6.45A. Bruker AXS Inc., Madison, Wisconsin, USA.

Claborn, K., Puklin-Faucher, E., Kurimoto, M., Kaminsky, W. & Kahr, B. (2003). *J. Am. Chem. Soc.* **125**, 1425–14831.

Hypercube (2000). *HYPERCHEM*. Release 6.01 for Windows. Hypercube Inc., Waterloo, Ontario, Canada.

Jagannadham, A. V. (1957). *Z. Kristallogr.* **108**, 457–458.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Prakash, A. (1962). *Ind. J. Phys.* **36**, 654–656.

Prakash, A. (1965). *Z. Kristallogr.* **122**, 272–282.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Smulevich, G., Guarini, G. G. T. & Marzocchi, M. P. (1987). *Mol. Cryst. Liq. Cryst.* **142**, 173–179.

Smulevich, G. & Marzocchi, M. P. (1985). *Chem. Phys.* **94**, 99–108.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.