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1,8-Dihydroxy-2,4,5,7-tetranitro-9,10-anthraquinone

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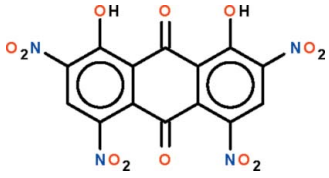
Key indicators: single-crystal X-ray study; T = 223 K; mean σ(C–C) = 0.004 Å; R factor = 0.063; wR factor = 0.215; data-to-parameter ratio = 9.6.

The ring system in the title compound, $C_{14}H_4N_4O_{12}$, is essentially planar (r.m.s. deviation of the carbon atoms = 0.085 Å); the two hydroxy groups form intramolecular hydrogen bonds to the same carbonyl O atom. The nitro groups are twisted with respect to the mean plane of the ring system by 74.3 (1) (1-nitro), 42.3 (3) (3-nitro), 45.7 (3) (6-nitro) and 66.9 (1)° (8-nitro).

Related literature

For the synthesis of the title compound, see: Teich *et al.* (2004). For related structures, see: Armaghan *et al.* (2010); Brown & Colclough (1983), Yatsenko *et al.* (1996).



Experimental

Crystal data

$C_{14}H_4N_4O_{12}$
M_r = 420.21
Monoclinic, $P2_1/c$
a = 17.726 (2) Å
b = 9.007 (1) Å
c = 9.731 (1) Å
β = 102.643 (2)°
V = 1515.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 223 K
0.35 × 0.25 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
11323 measured reflections
2672 independent reflections
2034 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.215
S = 1.10
2672 reflections
279 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.84 (3)	1.84 (3)	2.579 (3)	146 (5)
O3—H3···O2	0.84 (4)	1.82 (3)	2.576 (3)	148 (5)

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); 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, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5249).

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supporting information

Acta Cryst. (2010). E**66**, o1164 [https://doi.org/10.1107/S1600536810014431]

1,8-Dihydroxy-2,4,5,7-tetranitro-9,10-anthraquinone

Mahsa Armaghan, Mostafa M. Amini and Seik Weng Ng

S1. Comment

In continuation to our previous synthesis of anthraquinone derivatives for the absorption of aromatic sulfur compounds from oil when immobilized on silica surface (MCM-41) (Armaghan *et al.*, 2010), we have synthesized the title compound. The compound was reported in a previous report (Teich *et al.*, 2004). In the present study, the synthesis involves functionalization of 1,8-dihydroxy-anthraquinone with the fuming nitric acid. The compound (Scheme I, Fig. 1) is soluble in methanol.

S2. Experimental

Fuming nitric acid (4 ml) was added to a solution of 1,8-dihydroxy-anthraquinone (240 mg, 1.0 mmol) dissolved in concentrated sulfuric acid (5 ml). The mixture was stirred for 2 hours. It was then poured into ice (100 g). The yellow precipitate was washed with water. Crystals were obtained by slow diffusion of *n*-hexane into a methanol solution of the title compound; m.p.> 473 K.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.94 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C). The oxygen-bound H-atoms were located in a difference Fourier map. They were refined isotropically with a distance restraint of O–H 0.84±0.01 Å.

The parameters in the weighting scheme are somewhat large; these could not be reduced without affecting the goodness of fit.

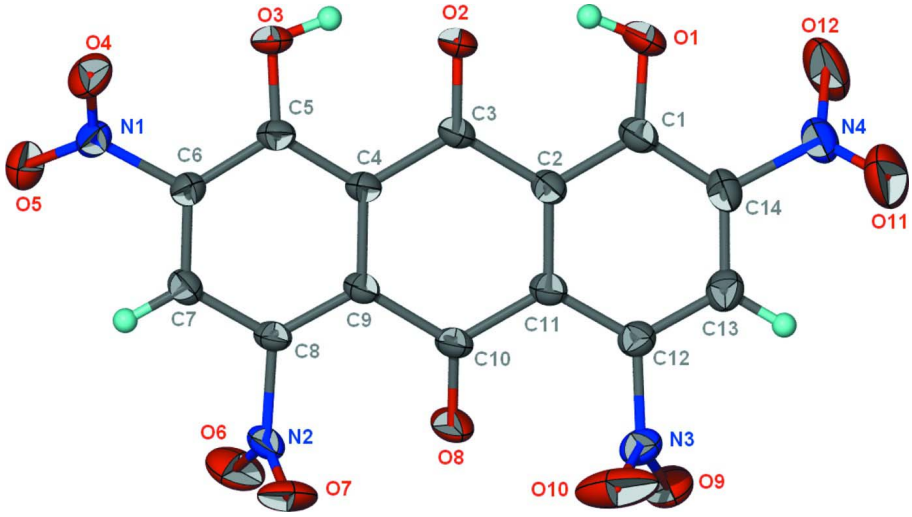

Figure 1

Anisotropic displacement ellipsoid plot (Barbour, 2001) of $C_{14}H_4N_4O_{12}$; ellipsoids are drawn at the 50% probability level and H atoms are of arbitrary radius.

1,8-Dihydroxy-2,4,5,7-tetranitro-9,10-anthraquinone

Crystal data

$C_{14}H_4N_4O_{12}$
$M_r = 420.21$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 17.726$ (2) Å
$b = 9.007$ (1) Å
$c = 9.731$ (1) Å
$\beta = 102.643$ (2)°
$V = 1515.9$ (3) Å^3
$Z = 4$
$F(000) = 848$
$D_x = 1.841$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2323 reflections
$\theta = 2.3$–$27.5°$
$\mu = 0.17$ mm^{-1}
$T = 223$ K
Plate, brown
0.35 × 0.25 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Graphite monochromator
ω scans
11323 measured reflections
2672 independent reflections
2034 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.2°$
$h = -19 \rightarrow 21$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.215$
$S = 1.10$
2672 reflections
279 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.137P)^2 + 0.3859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.34937 (16)	0.2030 (3)	0.4649 (3)	0.0528 (7)
H1	0.323 (2)	0.172 (5)	0.388 (3)	0.082 (16)*
O2	0.24924 (13)	0.2174 (2)	0.2291 (2)	0.0417 (6)
O3	0.15091 (14)	0.2212 (2)	−0.0089 (3)	0.0410 (6)
H3	0.183 (2)	0.186 (6)	0.060 (4)	0.099 (18)*
O4	0.07048 (14)	0.2831 (3)	−0.2661 (3)	0.0503 (7)
O5	−0.02307 (13)	0.4233 (3)	−0.2381 (3)	0.0465 (7)
O6	0.06528 (16)	0.8754 (3)	0.0919 (3)	0.0606 (8)
O7	0.17014 (16)	0.9106 (3)	0.0217 (3)	0.0565 (8)
O8	0.22018 (17)	0.7979 (3)	0.2950 (3)	0.0614 (9)
O9	0.33793 (14)	0.8827 (3)	0.5708 (3)	0.0507 (7)
O10	0.3791 (2)	0.8835 (3)	0.3801 (4)	0.0895 (12)
O11	0.51679 (18)	0.4003 (4)	0.7123 (4)	0.0879 (12)
O12	0.43047 (19)	0.2420 (4)	0.7288 (3)	0.0806 (11)
N1	0.04326 (15)	0.3791 (3)	−0.2055 (3)	0.0333 (6)
N2	0.12252 (16)	0.8324 (3)	0.0558 (3)	0.0348 (6)
N3	0.35601 (16)	0.8218 (3)	0.4727 (3)	0.0413 (7)
N4	0.45331 (17)	0.3494 (3)	0.6774 (3)	0.0438 (7)
C1	0.34783 (18)	0.3492 (4)	0.4612 (3)	0.0348 (7)
C2	0.29723 (16)	0.4320 (3)	0.3556 (3)	0.0293 (7)
C3	0.24621 (16)	0.3536 (3)	0.2380 (3)	0.0305 (7)
C4	0.19253 (16)	0.4400 (3)	0.1305 (3)	0.0279 (7)
C5	0.14731 (17)	0.3649 (3)	0.0136 (3)	0.0292 (7)
C6	0.09371 (17)	0.4510 (3)	−0.0830 (3)	0.0295 (7)
C7	0.08449 (17)	0.5998 (3)	−0.0660 (3)	0.0303 (7)
H7	0.0465	0.6532	−0.1295	0.036*
C8	0.13215 (16)	0.6704 (3)	0.0466 (3)	0.0284 (7)
C9	0.18590 (16)	0.5934 (3)	0.1447 (3)	0.0270 (7)
C10	0.23464 (18)	0.6727 (3)	0.2673 (3)	0.0326 (7)
C11	0.29712 (17)	0.5868 (3)	0.3616 (3)	0.0296 (7)
C12	0.35047 (17)	0.6585 (4)	0.4664 (3)	0.0324 (7)
C13	0.40121 (18)	0.5807 (4)	0.5685 (3)	0.0374 (8)
H13	0.4371	0.6309	0.6386	0.045*
C14	0.39833 (18)	0.4294 (4)	0.5659 (3)	0.0374 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0710 (18)	0.0263 (13)	0.0517 (16)	0.0112 (11)	−0.0070 (13)	0.0058 (11)
O2	0.0511 (14)	0.0192 (12)	0.0471 (14)	0.0043 (9)	−0.0062 (11)	0.0007 (9)
O3	0.0589 (16)	0.0178 (11)	0.0410 (13)	−0.0005 (10)	−0.0008 (11)	−0.0021 (9)
O4	0.0553 (16)	0.0469 (15)	0.0447 (14)	0.0009 (12)	0.0024 (11)	−0.0179 (12)
O5	0.0356 (13)	0.0538 (15)	0.0459 (14)	−0.0033 (11)	−0.0002 (10)	−0.0021 (11)
O6	0.0752 (19)	0.0413 (15)	0.0698 (19)	0.0242 (13)	0.0254 (15)	0.0017 (12)
O7	0.0714 (18)	0.0215 (12)	0.080 (2)	−0.0048 (12)	0.0241 (15)	0.0037 (12)

O8	0.094 (2)	0.0270 (14)	0.0471 (15)	0.0208 (13)	−0.0187 (14)	−0.0113 (11)
O9	0.0628 (16)	0.0403 (14)	0.0484 (15)	0.0035 (11)	0.0108 (12)	−0.0159 (11)
O10	0.174 (4)	0.0379 (16)	0.074 (2)	−0.0259 (18)	0.066 (2)	−0.0057 (14)
O11	0.057 (2)	0.092 (3)	0.097 (3)	0.0004 (17)	−0.0214 (18)	0.020 (2)
O12	0.075 (2)	0.089 (2)	0.067 (2)	0.0012 (17)	−0.0084 (16)	0.0411 (18)
N1	0.0357 (15)	0.0309 (14)	0.0308 (13)	−0.0076 (11)	0.0020 (11)	0.0005 (11)
N2	0.0458 (16)	0.0257 (14)	0.0300 (13)	0.0127 (12)	0.0018 (11)	0.0004 (11)
N3	0.0558 (17)	0.0317 (15)	0.0339 (15)	−0.0049 (13)	0.0047 (13)	−0.0061 (12)
N4	0.0417 (17)	0.0464 (18)	0.0391 (16)	0.0086 (13)	−0.0002 (13)	0.0057 (13)
C1	0.0400 (17)	0.0286 (17)	0.0348 (16)	0.0070 (13)	0.0064 (13)	0.0033 (12)
C2	0.0344 (16)	0.0266 (16)	0.0262 (15)	0.0051 (12)	0.0052 (12)	0.0020 (11)
C3	0.0357 (17)	0.0223 (17)	0.0321 (16)	0.0040 (11)	0.0045 (13)	0.0021 (12)
C4	0.0301 (15)	0.0205 (15)	0.0324 (15)	0.0006 (11)	0.0052 (12)	0.0015 (11)
C5	0.0361 (16)	0.0214 (15)	0.0307 (15)	−0.0014 (12)	0.0085 (12)	0.0007 (11)
C6	0.0315 (15)	0.0259 (16)	0.0297 (15)	−0.0030 (12)	0.0041 (12)	−0.0004 (12)
C7	0.0321 (16)	0.0291 (16)	0.0285 (15)	0.0032 (12)	0.0041 (12)	0.0043 (12)
C8	0.0348 (16)	0.0196 (15)	0.0310 (15)	0.0039 (12)	0.0078 (12)	0.0003 (12)
C9	0.0321 (15)	0.0218 (15)	0.0273 (15)	0.0037 (12)	0.0071 (12)	0.0019 (11)
C10	0.0457 (18)	0.0206 (16)	0.0294 (15)	0.0046 (13)	0.0034 (13)	0.0000 (12)
C11	0.0377 (17)	0.0241 (16)	0.0272 (15)	0.0027 (12)	0.0073 (13)	0.0002 (11)
C12	0.0380 (16)	0.0294 (17)	0.0295 (15)	−0.0012 (13)	0.0064 (12)	−0.0019 (12)
C13	0.0398 (18)	0.0413 (19)	0.0297 (16)	−0.0005 (14)	0.0047 (13)	−0.0039 (13)
C14	0.0355 (17)	0.042 (2)	0.0319 (17)	0.0073 (14)	0.0019 (13)	0.0037 (14)

Geometric parameters (Å, º)

O1—C1	1.317 (4)	C1—C14	1.401 (4)
O1—H1	0.84 (3)	C1—C2	1.419 (4)
O2—C3	1.232 (4)	C2—C11	1.395 (4)
O3—C5	1.316 (4)	C2—C3	1.474 (4)
O3—H3	0.84 (4)	C3—C4	1.473 (4)
O4—N1	1.206 (3)	C4—C9	1.396 (4)
O5—N1	1.216 (3)	C4—C5	1.412 (4)
O6—N2	1.208 (4)	C5—C6	1.413 (4)
O7—N2	1.201 (4)	C6—C7	1.364 (4)
O8—C10	1.199 (4)	C7—C8	1.383 (4)
O9—N3	1.203 (4)	C7—H7	0.9400
O10—N3	1.205 (4)	C8—C9	1.379 (4)
O11—N4	1.194 (4)	C9—C10	1.493 (4)
O12—N4	1.199 (4)	C10—C11	1.491 (4)
N1—C6	1.475 (4)	C11—C12	1.389 (4)
N2—C8	1.474 (4)	C12—C13	1.377 (4)
N3—C12	1.474 (4)	C13—C14	1.364 (4)
N4—C14	1.478 (4)	C13—H13	0.9400
C1—O1—H1	108 (4)	C4—C5—C6	116.9 (3)
C5—O3—H3	107 (4)	C7—C6—C5	122.7 (3)
O4—N1—O5	125.1 (3)	C7—C6—N1	117.5 (2)

O4—N1—C6	118.3 (2)	C5—C6—N1	119.8 (3)
O5—N1—C6	116.6 (3)	C6—C7—C8	118.6 (3)
O7—N2—O6	125.3 (3)	C6—C7—H7	120.7
O7—N2—C8	117.8 (3)	C8—C7—H7	120.7
O6—N2—C8	116.8 (3)	C9—C8—C7	121.8 (3)
O9—N3—O10	125.2 (3)	C9—C8—N2	121.9 (2)
O9—N3—C12	117.4 (3)	C7—C8—N2	116.4 (2)
O10—N3—C12	117.4 (3)	C8—C9—C4	119.3 (3)
O11—N4—O12	125.1 (3)	C8—C9—C10	120.2 (3)
O11—N4—C14	116.7 (3)	C4—C9—C10	120.4 (2)
O12—N4—C14	118.1 (3)	O8—C10—C11	121.1 (3)
O1—C1—C14	119.3 (3)	O8—C10—C9	121.0 (3)
O1—C1—C2	123.4 (3)	C11—C10—C9	117.7 (3)
C14—C1—C2	117.2 (3)	C12—C11—C2	119.3 (3)
C11—C2—C1	120.1 (3)	C12—C11—C10	120.3 (3)
C11—C2—C3	120.3 (2)	C2—C11—C10	120.0 (2)
C1—C2—C3	119.6 (3)	C13—C12—C11	121.7 (3)
O2—C3—C4	120.5 (3)	C13—C12—N3	116.8 (3)
O2—C3—C2	120.2 (3)	C11—C12—N3	121.6 (3)
C4—C3—C2	119.3 (3)	C14—C13—C12	118.6 (3)
C9—C4—C5	120.6 (3)	C14—C13—H13	120.7
C9—C4—C3	120.5 (3)	C12—C13—H13	120.7
C5—C4—C3	118.9 (3)	C13—C14—C1	123.0 (3)
O3—C5—C4	124.4 (3)	C13—C14—N4	117.3 (3)
O3—C5—C6	118.6 (3)	C1—C14—N4	119.7 (3)

O1—C1—C2—C11	177.7 (3)	C5—C4—C9—C8	2.9 (4)
C14—C1—C2—C11	−2.4 (4)	C3—C4—C9—C8	−176.4 (3)
O1—C1—C2—C3	−3.7 (5)	C5—C4—C9—C10	−179.1 (3)
C14—C1—C2—C3	176.3 (3)	C3—C4—C9—C10	1.6 (4)
C11—C2—C3—O2	176.3 (3)	C8—C9—C10—O8	11.7 (5)
C1—C2—C3—O2	−2.3 (4)	C4—C9—C10—O8	−166.3 (3)
C11—C2—C3—C4	−2.8 (4)	C8—C9—C10—C11	−173.9 (3)
C1—C2—C3—C4	178.6 (3)	C4—C9—C10—C11	8.1 (4)
O2—C3—C4—C9	176.3 (3)	C1—C2—C11—C12	4.3 (4)
C2—C3—C4—C9	−4.5 (4)	C3—C2—C11—C12	−174.3 (3)
O2—C3—C4—C5	−3.0 (4)	C1—C2—C11—C10	−168.6 (3)
C2—C3—C4—C5	176.1 (3)	C3—C2—C11—C10	12.8 (4)
C9—C4—C5—O3	178.9 (3)	O8—C10—C11—C12	−13.8 (5)
C3—C4—C5—O3	−1.8 (4)	C9—C10—C11—C12	171.8 (3)
C9—C4—C5—C6	−2.6 (4)	O8—C10—C11—C2	159.0 (3)
C3—C4—C5—C6	176.7 (3)	C9—C10—C11—C2	−15.4 (4)
O3—C5—C6—C7	178.2 (3)	C2—C11—C12—C13	−3.0 (5)
C4—C5—C6—C7	−0.5 (4)	C10—C11—C12—C13	169.9 (3)
O3—C5—C6—N1	0.2 (4)	C2—C11—C12—N3	176.3 (3)
C4—C5—C6—N1	−178.5 (2)	C10—C11—C12—N3	−10.8 (4)
O4—N1—C6—C7	142.1 (3)	O9—N3—C12—C13	−67.5 (4)
O5—N1—C6—C7	−37.2 (4)	O10—N3—C12—C13	111.6 (4)

O4—N1—C6—C5	−39.8 (4)	O9—N3—C12—C11	113.1 (3)
O5—N1—C6—C5	140.9 (3)	O10—N3—C12—C11	−67.7 (4)
C5—C6—C7—C8	3.2 (4)	C11—C12—C13—C14	−0.2 (5)
N1—C6—C7—C8	−178.8 (3)	N3—C12—C13—C14	−179.6 (3)
C6—C7—C8—C9	−2.9 (4)	C12—C13—C14—C1	2.2 (5)
C6—C7—C8—N2	176.9 (3)	C12—C13—C14—N4	−179.7 (3)
O7—N2—C8—C9	76.1 (4)	O1—C1—C14—C13	179.0 (3)
O6—N2—C8—C9	−106.8 (3)	C2—C1—C14—C13	−1.0 (5)
O7—N2—C8—C7	−103.7 (3)	O1—C1—C14—N4	1.0 (5)
O6—N2—C8—C7	73.4 (3)	C2—C1—C14—N4	−179.0 (3)
C7—C8—C9—C4	−0.1 (4)	O11—N4—C14—C13	−38.1 (5)
N2—C8—C9—C4	−179.9 (3)	O12—N4—C14—C13	139.6 (4)
C7—C8—C9—C10	−178.1 (3)	O11—N4—C14—C1	140.0 (4)
N2—C8—C9—C10	2.1 (4)	O12—N4—C14—C1	−42.3 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84 (3)	1.84 (3)	2.579 (3)	146 (5)
O3—H3···O2	0.84 (4)	1.82 (3)	2.576 (3)	148 (5)