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1,5-Diamino-2,6-dibromo-9,10-anthraquinone

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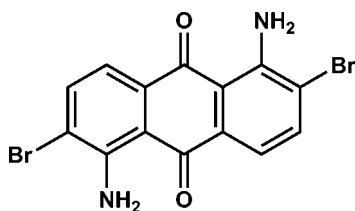
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Key indicators: single-crystal X-ray study; $T = 153$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.071; data-to-parameter ratio = 22.0.

In the title compound, $\text{C}_{14}\text{H}_8\text{Br}_2\text{N}_2\text{O}_2$, the molecular structure features intramolecular $\text{N}-\text{H}\cdots\text{O}$ [2.639 (2) Å and 130°] and $\text{N}-\text{H}\cdots\text{Br}$ [3.053 (2) Å and 114°] hydrogen bonding. Due to inversion symmetry, the asymmetric part of the unit cell consists of one half-molecule. In the crystal, inversion dimers linked by pairs of $\text{N}-\text{H}\cdots\text{O}$ [2.955 (2) Å and 135°] hydrogen bonds occur. The structure also features $\text{C}=\text{O}\cdots\pi$ [3.228 (2) Å] and $\text{Br}\cdots\text{Br}$ [3.569 (1) Å] contacts.

Related literature

For background information on anthraquinones and their pharmacological potential, see: Thomson (1967); Bohacova *et al.* (1998). For the X-ray structure of anthraquinone at different temperatures, see: Fu & Brock (1998). For a description of the resonance assisted hydrogen bond (RAHB) model, see: Gilli *et al.* (1989); Sanz *et al.* (2008). For structures with typical intramolecular $\text{N}-\text{H}\cdots\text{Br}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}=\text{O}\cdots\pi$ contacts, see: Brammer *et al.* (2001); Shimpi *et al.* (2007); Marten *et al.* (2007). For the synthetic procedure, see: Scholl & Krieger (1904).



Experimental

Crystal data

$\text{C}_{14}\text{H}_8\text{Br}_2\text{N}_2\text{O}_2$
 $M_r = 396.04$
 Triclinic, $P\bar{1}$
 $a = 4.4177$ (1) Å
 $b = 6.2240$ (2) Å
 $c = 11.8410$ (3) Å

$\alpha = 94.455$ (2)°
 $\beta = 99.970$ (2)°
 $\gamma = 100.859$ (2)°
 $V = 312.87$ (2) Å³
 $Z = 1$
 Mo $K\alpha$ radiation

$\mu = 6.48$ mm⁻¹
 $T = 153$ K

0.58 × 0.22 × 0.05 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\min} = 0.117$, $T_{\max} = 0.759$

7769 measured reflections
 2003 independent reflections
 1844 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.071$
 $S = 0.96$
 2003 reflections

91 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.86$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.63$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1B}\cdots\text{O1}$	0.88	1.99	2.639 (2)	130
$\text{N1}-\text{H1A}\cdots\text{Br1}$	0.88	2.59	3.053 (2)	114
$\text{N1}-\text{H1B}\cdots\text{O1}^i$	0.88	2.27	2.955 (2)	135

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2352).

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supporting information

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1,5-Diamino-2,6-dibromo-9,10-anthraquinone

Nadine Seidel, Wilhelm Seichter and Edwin Weber

S1. Comment

Anthraquinones represent the most important group of natural quinones (Thomson, 1967). They also find extensive application in chemical research and industry including aspects of pharmacology (Bohacova *et al.*, 1998). The title compound crystallizes in the triclinic space group $P\bar{1}$ with one half of the molecule in the asymmetric unit of the unit cell, i.e. the molecule adopts inversion symmetry. The anthraquinone part shows an almost planar geometry except for the bromo atoms which are slightly twisted out of the plane ($Cg(1)–C(1)–Br(1)$ 178.0 (2) °). Compared with the unsubstituted anthraquinone, the position of atoms shows distinct differences. The C—C bond lengths [$C(6)–C(7)$ 1.421 (2) Å, $C(1)–C(7)$ 1.420 (2) Å] are considerably elongated compared with 1.393 (2) Å, 1.381 (2) Å for anthraquinone. On the other hand, the angle of $C(6)–C(7)–C(1)$ 116.5 (2) ° is significantly reduced compared with 120.39 (14) ° for anthraquinone (Fu & Brock, 1998). This can be explained by the so called 'resonance assisted hydrogen bond (RAHB) model', which is based on the assumption of a synergistic mutual reinforcement of intramolecular hydrogen bonding due to the conjugation of π electrons (Gilli *et al.*, 1989). In our case, the amino group of the molecule seems to be involved in an intramolecular hydrogen bond of this type [$N1–H1B\cdots O1$ 2.639 (2) Å, 130 °]. However, this particular conception is also disputed (Sanz *et al.*, 2008). The amino group is also involved in an intramolecular N—H \cdots Br contact [$N1–H1A\cdots Br1$ 3.053 (2) Å, 114 °] (Brammer *et al.*, 2001). In addition, intermolecular hydrogen bonds of the N—H \cdots O type are found [$N1–H1B\cdots O1$ 2.955 (3) Å, 135 °]. In with way tapes are generated, which are further cross-linked by Br \cdots Br-contacts [$Br\cdots Br$ 3.569 (1) Å, 155.8 (1) °] (Shimpi *et al.*, 2007). The resulting two-dimensional networks are stacked *via* C=O $\cdots\pi$ interactions [$C(5)\cdots Cg(2)$ 3.228 (2) Å, 97.28 (13) °] (Marten *et al.*, 2007).

S2. Experimental

The title compound was synthesized by bromination of 1,5-diaminoanthra-9,10-quinone (1.0 g, 4.20 mmol) with bromine in acetic acid. For the synthetic procedure, see: Scholl & Krieger (1904). Purification by column chromatography (silica gel, *n*-hexane:ethyl acetate/4:1) followed by crystallization from toluene yielded 1.1 g (68%) of the compound as red prismatic crystals.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aryl and N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$ for amino atoms.

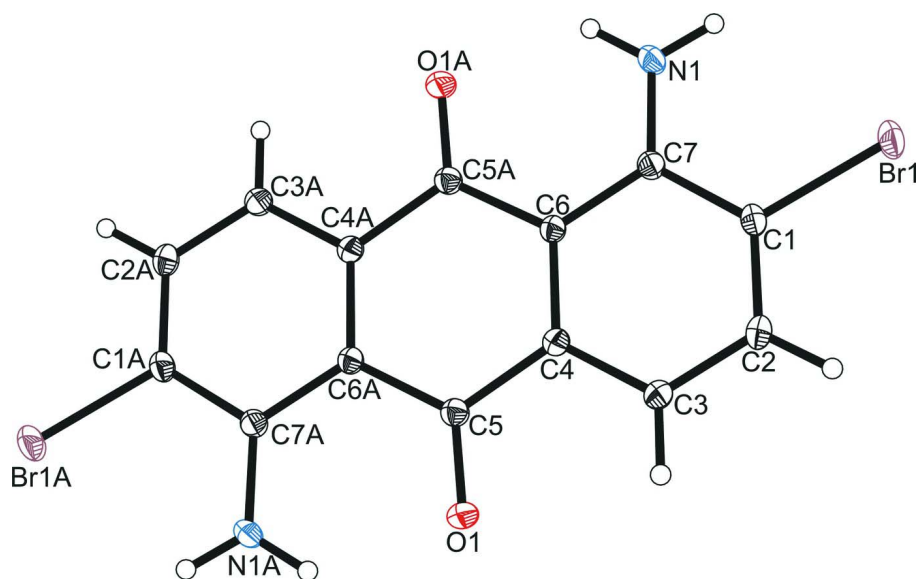


Figure 1

Perspective view of the title compound, showing 50% probability displacement ellipsoids for non-H atoms.

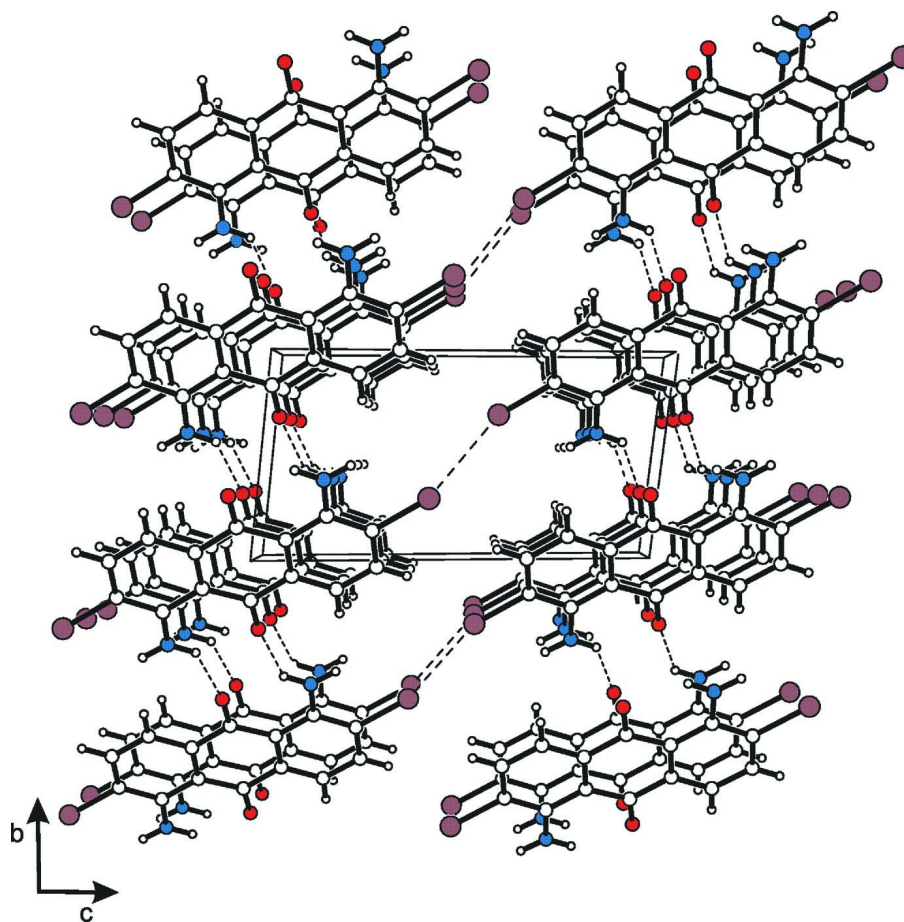


Figure 2

Packing diagram of the title compound viewed down the a axis. Intermolecular contacts are shown as dashed lines.

1,5-Diamino-2,6-dibromo-9,10-anthraquinone

Crystal data

$C_{14}H_8Br_2N_2O_2$

$M_r = 396.04$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 4.4177$ (1) Å

$b = 6.2240$ (2) Å

$c = 11.8410$ (3) Å

$\alpha = 94.455$ (2)°

$\beta = 99.970$ (2)°

$\gamma = 100.859$ (2)°

$V = 312.87$ (2) Å³

$Z = 1$

$F(000) = 192$

$D_x = 2.102$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5166 reflections

$\theta = 3.2$ – 38.8 °

$\mu = 6.48$ mm⁻¹

$T = 153$ K

Irregular, red

$0.58 \times 0.22 \times 0.05$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.117$, $T_{\max} = 0.759$

7769 measured reflections

2003 independent reflections

1844 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 31.1$ °, $\theta_{\min} = 3.4$ °

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.071$

$S = 0.96$

2003 reflections

91 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

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.2515P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.86$ e Å⁻³

$\Delta\rho_{\min} = -0.63$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.18844 (5)	0.30597 (3)	0.572710 (15)	0.02812 (8)

O1	0.1853 (3)	0.3189 (2)	1.04118 (13)	0.0228 (3)
N1	0.1114 (4)	0.3920 (3)	0.82251 (13)	0.0197 (3)
H1A	0.0439	0.4563	0.7622	0.024*
H1B	0.0777	0.4351	0.8910	0.024*
C1	0.3215 (4)	0.1566 (3)	0.69978 (14)	0.0184 (3)
C2	0.4697 (4)	-0.0157 (3)	0.68165 (15)	0.0205 (3)
H2	0.4972	-0.0606	0.6062	0.025*
C3	0.5785 (4)	-0.1235 (3)	0.77398 (15)	0.0188 (3)
H3	0.6811	-0.2421	0.7618	0.023*
C4	0.5371 (4)	-0.0574 (3)	0.88430 (14)	0.0152 (3)
C5	0.3340 (4)	0.1755 (3)	1.02023 (15)	0.0159 (3)
C6	0.3806 (4)	0.1154 (3)	0.90319 (14)	0.0145 (3)
C7	0.2662 (4)	0.2273 (3)	0.80995 (14)	0.0158 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04356 (14)	0.03062 (12)	0.01527 (11)	0.01733 (9)	0.00600 (8)	0.00918 (7)
O1	0.0304 (7)	0.0252 (7)	0.0177 (6)	0.0166 (5)	0.0062 (5)	0.0020 (5)
N1	0.0264 (7)	0.0191 (7)	0.0164 (7)	0.0110 (6)	0.0032 (5)	0.0048 (5)
C1	0.0223 (7)	0.0205 (8)	0.0132 (7)	0.0063 (6)	0.0027 (5)	0.0042 (6)
C2	0.0257 (8)	0.0246 (8)	0.0123 (7)	0.0074 (6)	0.0045 (6)	0.0019 (6)
C3	0.0249 (8)	0.0185 (7)	0.0152 (7)	0.0090 (6)	0.0050 (6)	0.0011 (6)
C4	0.0161 (7)	0.0162 (7)	0.0138 (7)	0.0044 (5)	0.0030 (5)	0.0012 (5)
C5	0.0167 (7)	0.0154 (7)	0.0156 (7)	0.0041 (5)	0.0027 (5)	0.0016 (6)
C6	0.0161 (7)	0.0150 (7)	0.0127 (7)	0.0038 (5)	0.0026 (5)	0.0011 (5)
C7	0.0173 (7)	0.0154 (7)	0.0150 (7)	0.0038 (5)	0.0027 (5)	0.0019 (5)

Geometric parameters (Å, °)

Br1—C1	1.8949 (18)	C2—H2	0.9500
O1—C5	1.238 (2)	C3—C4	1.392 (2)
N1—C7	1.348 (2)	C3—H3	0.9500
N1—H1A	0.8800	C4—C6	1.407 (2)
N1—H1B	0.8800	C5—C6	1.467 (2)
C1—C2	1.379 (3)	C5—C4 ⁱ	1.485 (2)
C1—C7	1.420 (2)	C6—C7	1.421 (2)
C2—C3	1.389 (3)		
C7—N1—H1A	120.0	C3—C4—C6	120.66 (16)
C7—N1—H1B	120.0	C3—C4—C5 ⁱ	117.24 (15)
H1A—N1—H1B	120.0	C6—C4—C5 ⁱ	122.10 (15)
C2—C1—C7	122.64 (16)	O1—C5—C6	121.83 (16)
C2—C1—Br1	118.66 (13)	O1—C5—C4 ⁱ	119.18 (16)
C7—C1—Br1	118.69 (13)	C6—C5—C4 ⁱ	118.98 (15)
C1—C2—C3	119.84 (16)	C4—C6—C7	120.42 (15)
C1—C2—H2	120.1	C4—C6—C5	118.89 (15)
C3—C2—H2	120.1	C7—C6—C5	120.69 (15)

C2—C3—C4	119.87 (16)	N1—C7—C1	120.38 (16)
C2—C3—H3	120.1	N1—C7—C6	123.08 (15)
C4—C3—H3	120.1	C1—C7—C6	116.54 (15)
Br1—Br1—C1—C2	0.00 (9)	O1—C5—C6—C4	-176.53 (16)
Br1—Br1—C1—C7	0.00 (10)	C4 ⁱ —C5—C6—C4	2.1 (2)
C7—C1—C2—C3	-1.7 (3)	O1—C5—C6—C7	2.6 (2)
Br1—C1—C2—C3	177.95 (14)	C4 ⁱ —C5—C6—C7	-178.77 (14)
C1—C2—C3—C4	0.1 (3)	C2—C1—C7—N1	-177.84 (17)
C2—C3—C4—C6	1.1 (3)	Br1—C1—C7—N1	2.5 (2)
C2—C3—C4—C5 ⁱ	-178.47 (16)	C2—C1—C7—C6	1.9 (2)
O1—O1—C5—C6	0.0 (5)	Br1—C1—C7—C6	-177.76 (12)
O1—O1—C5—C4 ⁱ	0.0 (6)	C4—C6—C7—N1	179.15 (16)
C3—C4—C6—C7	-0.9 (2)	C5—C6—C7—N1	0.0 (2)
C5 ⁱ —C4—C6—C7	178.70 (15)	C4—C6—C7—C1	-0.6 (2)
C3—C4—C6—C5	178.25 (15)	C5—C6—C7—C1	-179.71 (15)
C5 ⁱ —C4—C6—C5	-2.2 (3)		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1B...O1	0.88	1.99	2.639 (2)	130
N1—H1A...Br1	0.88	2.59	3.053 (2)	114
N1—H1B...O1 ⁱⁱ	0.88	2.27	2.955 (2)	135

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