

(1*R*,2*R*)/(1*S*,2*S*)-1,2-Bis(2-hydroxyphenyl)ethylenediammonium dibromide monohydrateHae-Jo Kim,^a Alan J. Lough^{b*} and Jik Chin^b^aDepartment of Chemistry, Kyonggi University, Suwon 443-760, Republic of Korea, and ^bDepartment of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6Correspondence e-mail: alough@chem.utoronto.ca

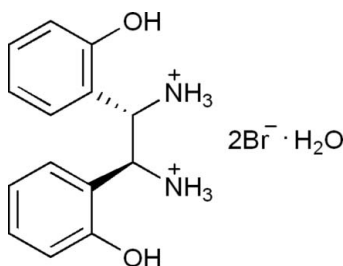
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; H-atom completeness 91%; disorder in solvent or counterion; R factor = 0.052; wR factor = 0.153; data-to-parameter ratio = 15.3.

In the cation of the title compound, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2^{2+} \cdot 2\text{Br}^- \cdot \text{H}_2\text{O}$, the two H atoms attached to the two sp^3 -hybridized C atoms are in an anti orientation with respect to each other and the dihedral angle between the two benzene rings is 49.5 (2)°. The crystal structure is stabilized by $\text{O}-\text{H} \cdots \text{Br}$ and $\text{N}-\text{H} \cdots \text{Br}$ hydrogen bonds. The solvent O atom is disordered equally over three positions.

Related literature

For background information, see: Kim, Kim, Alhakimi *et al.* (2005); Kim, Kim, Lough *et al.* (2005); Kim *et al.* (2006). For other related literature, see: Bryant *et al.* (2002); Gust & Schönerberger (1993); Lucet *et al.* (1998).

**Experimental***Crystal data* $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2^{2+} \cdot 2\text{Br}^- \cdot \text{H}_2\text{O}$ $M_r = 424.14$ Monoclinic, $P2_1/c$ $a = 5.4499$ (5) Å $b = 16.883$ (2) Å $c = 20.042$ (2) Å $\beta = 95.321$ (8)° $V = 1836.1$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 4.43$ mm⁻¹ $T = 293$ (2) K $0.36 \times 0.26 \times 0.03$ mm*Data collection*

Nonius KappaCCD diffractometer

Absorption correction: multi-scan

(SORTAV; Blessing, 1995)

 $T_{\min} = 0.465$, $T_{\max} = 0.855$

10004 measured reflections

3233 independent reflections

2162 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.110$ *Refinement* $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.153$ $S = 1.03$

3233 reflections

211 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.57$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1} \cdots \text{Br2}^{\text{i}}$	0.82	2.43	3.217 (4)	160
$\text{O2}-\text{H2} \cdots \text{Br2}^{\text{ii}}$	0.82	2.42	3.194 (4)	157
$\text{N1}-\text{H1B} \cdots \text{Br2}^{\text{iii}}$	0.89	2.43	3.314 (5)	170
$\text{N1}-\text{H1C} \cdots \text{Br1}$	0.89	2.72	3.517 (5)	150
$\text{N1}-\text{H1D} \cdots \text{Br1}^{\text{ii}}$	0.89	2.46	3.285 (5)	155
$\text{N2}-\text{H2B} \cdots \text{Br2}$	0.89	2.45	3.330 (5)	168
$\text{N2}-\text{H2C} \cdots \text{Br1}^{\text{ii}}$	0.89	2.95	3.757 (5)	152
$\text{N2}-\text{H2D} \cdots \text{Br1}$	0.89	2.44	3.287 (5)	159

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

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2027).

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supplementary materials

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(1*R*,2*R*)/(1*S*,2*S*)-1,2-Bis(2-hydroxyphenyl)ethylenediammonium dibromide monohydrate

H.-J. Kim, A. J. Lough and J. Chin

Comment

Chiral vicinal diamines are found in a wide variety of stereoselective catalysts (Lucet *et al.*, 1998). We have shown that the title compound is very useful for making many chiral vicinal diamines in enantiomerically pure form by diaza-Cope rearrangement reaction (Kim, Kim, Alhakimi *et al.*, 2005; Kim, Kim, Lough *et al.*, 2005; Kim *et al.*, 2006). The crystal structure reveals that the two hydrogen atoms attached to the two sp^3 hybridized carbon are in an anti orientation with respect to each other while the two phenol groups and the two ammonium groups are in *gauche* orientations. Diimines formed between the title compound and aryl aldehydes also form the same conformer and are ideally pre-organized for the diaza-Cope rearrangement reaction. In contrast, in the structure of the *meso*-1,2-(2-hydroxyphenyl)-ethylenediamine (Bryant *et al.*, 2002) the hydrogen atoms, the phenols and the ammonium groups are all in anti orientations.

Experimental

The title compound was prepared according to a literature procedure (Gust & Schöenberger, 1993). Crystals suitable for X-ray diffraction were grown as colorless plates by slow diffusion of ethanol to a solution of the title compound in water over a period of 2 weeks. ^1H NMR (300 MHz, DMSO- d_6): 10.29 (s, 2H of OH); 8.50 (br s, 6H of NH_3); 7.09 (m, 4H of ArH); 6.80 (d, $^3J = 8.1$ Hz, 2H of ArH); 6.68 (t, $^3J = 7.5$ Hz, 2H of ArH); 5.19 (s, 2H of C*H).

Refinement

All hydrogen atoms were placed in calculated positions with C—H = 0.93 to 0.98 Å, N—H = 0.89 Å and O—H = 0.82 Å. They were included in the refinement in the riding-motion approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}} \text{ and } \text{O})$. A difference Fourier map revealed three peaks close to each other which were interpreted as a disordered O atom from a solvent H_2O molecule. This disordered water molecule was included in the refinement as three one third occupancy O atoms but the H atoms were not located or included. These H atoms are however included in the molecular formula.

Figures

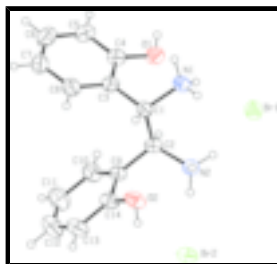


Fig. 1. The molecular structure with displacement ellipsoids drawn at the 30% probability level. The disordered water solvent molecule is not shown.

(1R,2R)/(1S,2S)-1,2-Bis(2-hydroxyphenyl)ethylenediammonium dibromide monohydrate

Crystal data

$C_{14}H_{18}N_2O_2^{2+} \cdot 2Br^- \cdot H_2O$

$M_r = 424.14$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.4499$ (5) Å

$b = 16.883$ (2) Å

$c = 20.042$ (2) Å

$\beta = 95.321$ (8)°

$V = 1836.1$ (3) Å³

$Z = 4$

$F_{000} = 848$

$D_x = 1.534$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 30763 reflections

$\theta = 2.6$ – 25.0 °

$\mu = 4.43$ mm⁻¹

$T = 293$ (2) K

Plate, colourless

$0.36 \times 0.26 \times 0.03$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 9 pixels mm⁻¹

$T = 293$ (2) K

φ scans, and ω scans with κ offsets

Absorption correction: multi-scan
(SORTAV; Blessing, 1995)

$T_{\min} = 0.465$, $T_{\max} = 0.855$

10004 measured reflections

3233 independent reflections

2162 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.110$

$\theta_{\max} = 25.0$ °

$\theta_{\min} = 2.6$ °

$h = -6 \rightarrow 6$

$k = -17 \rightarrow 20$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.153$

$S = 1.03$

3233 reflections

211 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0794P)^2]$

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

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

$\Delta\rho_{\max} = 0.57$ e Å⁻³

$\Delta\rho_{\min} = -0.45$ e Å⁻³

Extinction correction: SHELXTL (Sheldrick, 2001),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0034 (10)

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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	-0.02139 (12)	0.20389 (4)	0.14353 (3)	0.0609 (3)	
Br2	0.22244 (12)	-0.09688 (4)	0.17880 (4)	0.0618 (3)	
O1	0.1756 (8)	0.2625 (3)	0.3199 (2)	0.0627 (12)	
H1	0.0814	0.2971	0.3308	0.094*	
O2	0.8556 (8)	0.0179 (3)	0.2481 (2)	0.0656 (12)	
H2	0.9143	-0.0205	0.2302	0.098*	
N1	0.5375 (9)	0.2472 (3)	0.2386 (2)	0.0503 (12)	
H1B	0.5854	0.2928	0.2580	0.075*	
H1C	0.3762	0.2489	0.2266	0.075*	
H1D	0.6181	0.2395	0.2025	0.075*	
N2	0.4404 (10)	0.0871 (3)	0.1949 (2)	0.0537 (13)	
H2B	0.4033	0.0362	0.1882	0.081*	
H2C	0.5906	0.0965	0.1827	0.081*	
H2D	0.3312	0.1169	0.1706	0.081*	
C1	0.5929 (10)	0.1802 (3)	0.2873 (3)	0.0453 (13)	
H1A	0.7665	0.1655	0.2862	0.054*	
C2	0.4339 (10)	0.1066 (3)	0.2677 (3)	0.0457 (13)	
H2A	0.2631	0.1191	0.2753	0.055*	
C3	0.5552 (10)	0.2058 (3)	0.3577 (3)	0.0472 (14)	
C4	0.3491 (11)	0.2476 (4)	0.3722 (3)	0.0542 (15)	
C5	0.3219 (13)	0.2731 (4)	0.4373 (3)	0.0628 (17)	
H5A	0.1841	0.3022	0.4463	0.075*	
C6	0.5030 (15)	0.2544 (5)	0.4885 (3)	0.073 (2)	
H6A	0.4854	0.2713	0.5320	0.087*	
C7	0.7045 (15)	0.2121 (4)	0.4758 (4)	0.070 (2)	
H7A	0.8232	0.1994	0.5105	0.084*	
C8	0.7338 (13)	0.1876 (4)	0.4108 (3)	0.0604 (17)	
H8A	0.8730	0.1588	0.4022	0.072*	
C9	0.5135 (11)	0.0366 (3)	0.3109 (3)	0.0471 (14)	
C10	0.3794 (12)	0.0146 (4)	0.3634 (3)	0.0611 (17)	
H10A	0.2408	0.0436	0.3722	0.073*	
C11	0.4512 (15)	-0.0507 (5)	0.4033 (4)	0.082 (2)	
H11A	0.3621	-0.0646	0.4389	0.098*	

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C12	0.6536 (15)	-0.0946 (5)	0.3899 (5)	0.082 (2)	
H12A	0.6986	-0.1388	0.4159	0.098*	
C13	0.7897 (13)	-0.0735 (4)	0.3383 (4)	0.070 (2)	
H13A	0.9262	-0.1035	0.3295	0.084*	
C14	0.7238 (10)	-0.0074 (4)	0.2993 (3)	0.0536 (15)	
O1W	0.480 (6)	0.0574 (12)	0.0596 (8)	0.124 (9)	0.333
O2W	0.330 (6)	0.0251 (11)	0.0205 (9)	0.127 (10)	0.333
O3W	0.645 (4)	0.0134 (14)	0.0410 (9)	0.115 (7)	0.333

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0569 (4)	0.0658 (5)	0.0593 (4)	0.0077 (3)	0.0020 (3)	0.0038 (3)
Br2	0.0619 (4)	0.0403 (4)	0.0838 (5)	0.0006 (3)	0.0100 (3)	-0.0018 (3)
O1	0.056 (3)	0.063 (3)	0.069 (3)	0.013 (2)	-0.001 (2)	-0.011 (2)
O2	0.064 (3)	0.050 (3)	0.086 (3)	0.015 (2)	0.024 (2)	0.008 (2)
N1	0.053 (3)	0.040 (3)	0.058 (3)	-0.004 (2)	0.008 (2)	0.005 (2)
N2	0.063 (3)	0.044 (3)	0.053 (3)	0.004 (2)	0.001 (2)	-0.002 (2)
C1	0.043 (3)	0.041 (3)	0.051 (3)	0.000 (2)	0.000 (3)	0.004 (3)
C2	0.043 (3)	0.037 (3)	0.058 (3)	-0.001 (2)	0.010 (3)	-0.003 (3)
C3	0.045 (3)	0.043 (3)	0.054 (3)	-0.007 (3)	0.005 (3)	0.000 (3)
C4	0.050 (3)	0.048 (3)	0.065 (4)	0.000 (3)	0.005 (3)	-0.003 (3)
C5	0.067 (4)	0.058 (4)	0.064 (4)	-0.006 (3)	0.014 (4)	-0.014 (3)
C6	0.090 (5)	0.076 (5)	0.054 (4)	-0.015 (4)	0.014 (4)	-0.012 (4)
C7	0.084 (5)	0.068 (5)	0.056 (4)	-0.015 (4)	-0.010 (4)	0.007 (3)
C8	0.059 (4)	0.053 (4)	0.068 (4)	-0.009 (3)	-0.003 (3)	0.004 (3)
C9	0.051 (3)	0.037 (3)	0.054 (3)	-0.003 (3)	0.006 (3)	0.000 (3)
C10	0.060 (4)	0.055 (4)	0.069 (4)	-0.006 (3)	0.015 (3)	0.010 (3)
C11	0.080 (5)	0.080 (6)	0.088 (5)	-0.008 (4)	0.021 (4)	0.028 (5)
C12	0.072 (5)	0.071 (5)	0.100 (6)	-0.002 (4)	-0.003 (4)	0.030 (5)
C13	0.065 (4)	0.046 (4)	0.099 (6)	0.004 (3)	0.005 (4)	0.011 (4)
C14	0.043 (3)	0.041 (3)	0.076 (4)	-0.004 (3)	0.003 (3)	0.002 (3)
O1W	0.26 (3)	0.074 (12)	0.039 (9)	-0.018 (17)	0.047 (14)	-0.006 (8)
O2W	0.27 (3)	0.059 (11)	0.056 (11)	-0.026 (15)	0.030 (14)	0.003 (9)
O3W	0.132 (17)	0.135 (18)	0.073 (12)	0.030 (14)	-0.009 (12)	-0.042 (12)

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

O1—C4	1.368 (7)	C4—C5	1.394 (9)
O1—H1	0.8200	C5—C6	1.393 (10)
O2—C14	1.374 (7)	C5—H5A	0.9300
O2—H2	0.8200	C6—C7	1.354 (11)
N1—C1	1.507 (7)	C6—H6A	0.9300
N1—H1B	0.8900	C7—C8	1.390 (10)
N1—H1C	0.8900	C7—H7A	0.9300
N1—H1D	0.8900	C8—H8A	0.9300
N2—C2	1.500 (7)	C9—C10	1.386 (9)
N2—H2B	0.8900	C9—C14	1.403 (8)
N2—H2C	0.8900	C10—C11	1.396 (10)

N2—H2D	0.8900	C10—H10A	0.9300
C1—C3	1.508 (8)	C11—C12	1.376 (11)
C1—C2	1.544 (8)	C11—H11A	0.9300
C1—H1A	0.9800	C12—C13	1.374 (11)
C2—C9	1.506 (8)	C12—H12A	0.9300
C2—H2A	0.9800	C13—C14	1.391 (9)
C3—C4	1.380 (8)	C13—H13A	0.9300
C3—C8	1.407 (8)		
C4—O1—H1	109.5	C3—C4—C5	120.9 (6)
C14—O2—H2	109.5	C6—C5—C4	119.4 (7)
C1—N1—H1B	109.5	C6—C5—H5A	120.3
C1—N1—H1C	109.5	C4—C5—H5A	120.3
H1B—N1—H1C	109.5	C7—C6—C5	120.7 (7)
C1—N1—H1D	109.5	C7—C6—H6A	119.6
H1B—N1—H1D	109.5	C5—C6—H6A	119.6
H1C—N1—H1D	109.5	C6—C7—C8	120.0 (7)
C2—N2—H2B	109.5	C6—C7—H7A	120.0
C2—N2—H2C	109.5	C8—C7—H7A	120.0
H2B—N2—H2C	109.5	C7—C8—C3	120.7 (7)
C2—N2—H2D	109.5	C7—C8—H8A	119.6
H2B—N2—H2D	109.5	C3—C8—H8A	119.6
H2C—N2—H2D	109.5	C10—C9—C14	118.7 (6)
N1—C1—C3	110.8 (5)	C10—C9—C2	120.2 (5)
N1—C1—C2	111.4 (4)	C14—C9—C2	121.1 (5)
C3—C1—C2	110.3 (5)	C9—C10—C11	120.4 (7)
N1—C1—H1A	108.1	C9—C10—H10A	119.8
C3—C1—H1A	108.1	C11—C10—H10A	119.8
C2—C1—H1A	108.1	C12—C11—C10	120.1 (8)
N2—C2—C9	110.8 (4)	C12—C11—H11A	120.0
N2—C2—C1	111.2 (5)	C10—C11—H11A	120.0
C9—C2—C1	111.1 (5)	C13—C12—C11	120.4 (7)
N2—C2—H2A	107.9	C13—C12—H12A	119.8
C9—C2—H2A	107.9	C11—C12—H12A	119.8
C1—C2—H2A	107.9	C12—C13—C14	120.1 (7)
C4—C3—C8	118.2 (6)	C12—C13—H13A	120.0
C4—C3—C1	121.8 (5)	C14—C13—H13A	120.0
C8—C3—C1	119.9 (5)	O2—C14—C13	122.9 (6)
O1—C4—C3	116.8 (6)	O2—C14—C9	116.8 (5)
O1—C4—C5	122.2 (6)	C13—C14—C9	120.3 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...Br2 ⁱ	0.82	2.43	3.217 (4)	160
O2—H2...Br2 ⁱⁱ	0.82	2.42	3.194 (4)	157
N1—H1B...Br2 ⁱⁱⁱ	0.89	2.43	3.314 (5)	170
N1—H1C...Br1	0.89	2.72	3.517 (5)	150
N1—H1D...Br1 ⁱⁱ	0.89	2.46	3.285 (5)	155

supplementary materials

N2—H2B···Br2	0.89	2.45	3.330 (5)	168
N2—H2C···Br1 ⁱⁱ	0.89	2.95	3.757 (5)	152
N2—H2D···Br1	0.89	2.44	3.287 (5)	159

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

Fig. 1

