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1-(2-Bromoethyl)-1,4-diazoniabicyclo-[2.2.2]octane bromide dihydrogen phosphate–phosphoric acid (1/1)

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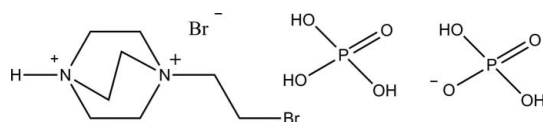
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.057; wR factor = 0.147; data-to-parameter ratio = 20.1.

In the crystal structure of the title compound, $\text{C}_8\text{H}_{17}\text{BrN}_2^{2+} \cdot \text{Br}^- \cdot \text{H}_2\text{PO}_4^- \cdot \text{H}_3\text{PO}_4$, the cations, anions and phosphoric acid molecules are linked by $\text{O}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{Br}$ hydrogen bonds into layers parallel to (101).

Related literature

For the dielectric properties of *N*-protonated compounds, see: Szafranski & Katrusiak (2008); Katrusiak & Szafranski (1999); Chen *et al.* (2008); Fu *et al.* (2009); Zhao *et al.* (2008).



Experimental

Crystal data

$\text{C}_8\text{H}_{17}\text{BrN}_2^{2+} \cdot \text{Br}^- \cdot \text{H}_2\text{PO}_4^- \cdot \text{H}_3\text{PO}_4$
 $M_r = 496.02$
 Monoclinic, $P2_1/c$
 $a = 12.963$ (3) Å
 $b = 7.5959$ (15) Å
 $c = 17.721$ (4) Å
 $\beta = 92.00$ (3)°

$V = 1743.9$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 4.87$ mm⁻¹
 $T = 293$ K
 $0.3 \times 0.25 \times 0.2$ mm

Data collection

Rigaku Mercury2 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.240$, $T_{\max} = 0.379$

17431 measured reflections
 3991 independent reflections
 3097 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.147$
 $S = 1.10$
 3991 reflections

199 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 1.03$ e Å⁻³
 $\Delta\rho_{\min} = -1.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1C} \cdots \text{O2}$	0.91	1.79	2.667 (6)	162
$\text{O1}-\text{H1D} \cdots \text{O6}$	0.82	1.71	2.519 (5)	170
$\text{O4}-\text{H4C} \cdots \text{O3}^i$	0.82	1.80	2.560 (5)	155
$\text{O5}-\text{H5C} \cdots \text{O3}^i$	0.82	1.73	2.555 (5)	179
$\text{O7}-\text{H7C} \cdots \text{O2}^{ii}$	0.82	1.77	2.555 (5)	159
$\text{O8}-\text{H8D} \cdots \text{Br1}^{iii}$	0.96	2.18	3.100 (4)	160

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, y, z + 1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

This work was supported by a start-up grant from Southeast University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2443).

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supporting information

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1-(2-Bromoethyl)-1,4-diazabicyclo[2.2.2]octane bromide dihydrogen phosphate–phosphoric acid (1/1)

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S1. Comment

The variable-temperature dielectric response, especially in relatively high frequency range, is very useful for searching phase transitions in which there is a dielectric anomaly at the transition temperature (Szafranski & Katrusiak, 2008; Katrusiak & Szafranski, 1999; Chen *et al.*, 2008; Fu *et al.*, 2009; Zhao *et al.*, 2008). Unluckily, the title compound, whose crystal structure is reported herein, has no dielectric disuniformity from 93 K to 400 K (m.p. = 410–412 K).

The asymmetric unit of the title compound (Fig. 1) consists of a 1-(2-bromoethyl)-1,4-diazabicyclo[2.2.2]octane-1,4-dium dication, a bromide anion, a dihydrogenphosphate anion and a phosphoric acid molecule. In the crystal packing (Fig. 2), intermolecular N—H \cdots O, O—H \cdots O and O—H \cdots Br hydrogen interactions (Table 1) link ions and molecules forming layers parallel to the (101) plane.

S2. Experimental

To a solution of 1,4-diazabicyclo[2.2.2]octane (5.6 g, 0.05 mol) in chloroform (20 ml) 1,2-dibromoethane (0.048 mol) was added in one portion and the mixture was refluxed for 8 hour. On standing for about 16 hour at room temperature, colourless hygroscopic crystals of 4-diazabicyclo[2.2.2]octan-1-ium bromide were obtained. The crude product was collected and dissolved in 20 ml methanol, then 1 M H₃PO₄ was dropped slowly with stirring. The white precipitate formed (yield 80%) was filtered and dissolved in the H₂O. After a few weeks, colourless hygroscopic block crystals of the title compound were obtained on slow evaporation of the solvent.

S3. Refinement

All the H atoms were calculated geometrically and refined using a riding model, with N—H = 0.90 Å, C—H = 0.97 Å, O—H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{O})$.

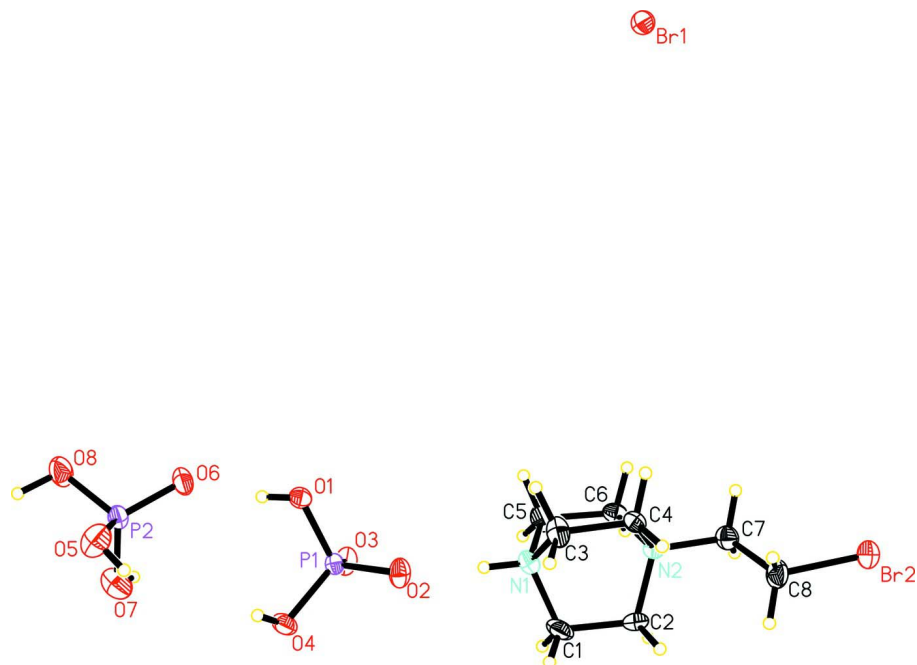


Figure 1

The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

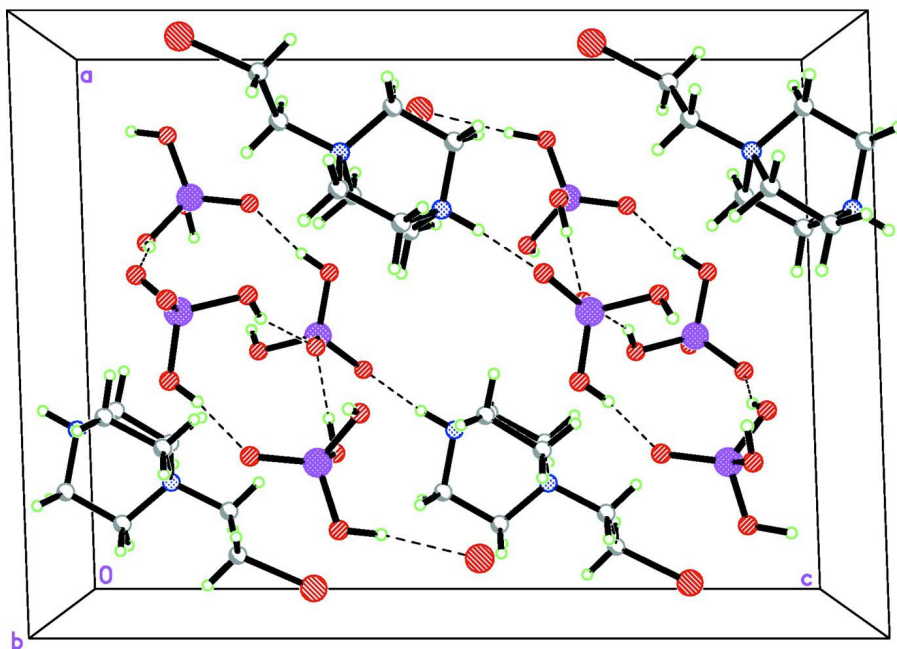


Figure 2

A view of the packing of the title compound, stacked along the *b* axis. Dashed lines indicate hydrogen bonds.

1-(2-Bromoethyl)-1,4-diazoniabicyclo[2.2.2]octane bromide dihydrogen phosphate–phosphoric acid (1/1)

Crystal data

$C_8H_{17}BrN_2^{2+} \cdot Br^- \cdot H_2PO_4^- \cdot H_3PO_4$
 $M_r = 496.02$
 Monoclinic, $P2_1/c$
 Hall symbol: -P 2ybc
 $a = 12.963 (3) \text{ \AA}$
 $b = 7.5959 (15) \text{ \AA}$
 $c = 17.721 (4) \text{ \AA}$
 $\beta = 92.00 (3)^\circ$
 $V = 1743.9 (7) \text{ \AA}^3$
 $Z = 4$

$F(000) = 992$
 $D_x = 1.889 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 7671 reflections
 $\theta = 3.4\text{--}27.5^\circ$
 $\mu = 4.87 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prism, colourless
 $0.3 \times 0.25 \times 0.2 \text{ mm}$

Data collection

Rigaku Mercury2
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 CCD_Profile_fitting scans
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.240$, $T_{\max} = 0.379$
 17431 measured reflections

3991 independent reflections
 3097 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$
 $h = -16 \rightarrow 16$
 $k = -9 \rightarrow 9$
 $l = -23 \rightarrow 22$
 1814 standard reflections

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.147$
 $S = 1.10$
 3991 reflections
 199 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
 $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 1.8668P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.03 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.30 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8045 (5)	0.7487 (8)	0.5147 (3)	0.0471 (14)
H1A	0.8221	0.6458	0.5450	0.057*
H1B	0.8240	0.8527	0.5436	0.057*
C2	0.8627 (4)	0.7443 (7)	0.4414 (3)	0.0352 (11)

H2A	0.9045	0.8496	0.4374	0.042*
H2B	0.9083	0.6431	0.4413	0.042*
C3	0.6645 (5)	0.9084 (8)	0.4485 (3)	0.0458 (14)
H3A	0.6851	1.0154	0.4748	0.055*
H3B	0.5905	0.9126	0.4387	0.055*
C4	0.7193 (4)	0.8955 (6)	0.3750 (2)	0.0283 (10)
H4A	0.7610	0.9999	0.3681	0.034*
H4B	0.6690	0.8887	0.3333	0.034*
C5	0.6608 (5)	0.5869 (8)	0.4562 (3)	0.0491 (15)
H5A	0.5875	0.5894	0.4434	0.059*
H5B	0.6748	0.4858	0.4885	0.059*
C6	0.7217 (4)	0.5720 (6)	0.3848 (3)	0.0323 (11)
H6A	0.7654	0.4684	0.3877	0.039*
H6B	0.6745	0.5591	0.3415	0.039*
C7	0.8408 (4)	0.7146 (7)	0.3008 (3)	0.0378 (12)
H7A	0.8807	0.6065	0.3019	0.045*
H7B	0.7888	0.7047	0.2603	0.045*
C8	0.9111 (5)	0.8654 (8)	0.2840 (3)	0.0492 (14)
H8A	0.9638	0.8778	0.3238	0.059*
H8B	0.8722	0.9743	0.2803	0.059*
N1	0.6916 (4)	0.7512 (5)	0.4966 (2)	0.0344 (10)
H1C	0.6570	0.7580	0.5404	0.041*
N2	0.7874 (3)	0.7339 (5)	0.3752 (2)	0.0262 (8)
O1	0.4055 (3)	0.7844 (4)	0.65616 (19)	0.0342 (8)
H1D	0.3713	0.7503	0.6914	0.051*
O2	0.5835 (3)	0.8397 (4)	0.6163 (2)	0.0407 (9)
O3	0.5392 (3)	0.5469 (4)	0.6708 (2)	0.0401 (9)
O4	0.5490 (3)	0.8038 (5)	0.7549 (2)	0.0438 (9)
H4C	0.5100	0.8835	0.7667	0.066*
O5	0.2784 (3)	0.9370 (5)	0.8525 (3)	0.0589 (11)
H5C	0.3371	0.9707	0.8448	0.088*
O6	0.2824 (3)	0.6928 (6)	0.7558 (2)	0.0578 (12)
O7	0.3544 (4)	0.6584 (6)	0.8901 (2)	0.0622 (12)
H7C	0.3639	0.5548	0.8794	0.093*
O8	0.1613 (4)	0.6852 (7)	0.8600 (2)	0.0734 (15)
H8D	0.1511	0.7297	0.9099	0.110*
Br1	0.11078 (4)	0.73719 (7)	0.02823 (3)	0.03808 (18)
Br2	0.97424 (5)	0.81384 (9)	0.18848 (3)	0.0491 (2)
P1	0.52097 (10)	0.74245 (15)	0.67295 (7)	0.0260 (3)
P2	0.26999 (11)	0.73716 (17)	0.83560 (8)	0.0336 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.053 (4)	0.061 (4)	0.027 (3)	-0.003 (3)	-0.015 (2)	0.004 (2)
C2	0.027 (3)	0.037 (3)	0.041 (3)	-0.001 (2)	-0.010 (2)	-0.003 (2)
C3	0.054 (3)	0.045 (3)	0.039 (3)	0.018 (3)	0.011 (3)	0.008 (2)
C4	0.034 (3)	0.025 (2)	0.026 (2)	0.0043 (19)	-0.0025 (19)	0.0012 (18)

C5	0.064 (4)	0.044 (3)	0.040 (3)	-0.024 (3)	0.007 (3)	-0.005 (3)
C6	0.038 (3)	0.023 (2)	0.035 (3)	-0.004 (2)	-0.008 (2)	-0.0012 (19)
C7	0.040 (3)	0.038 (3)	0.035 (3)	0.004 (2)	0.004 (2)	-0.008 (2)
C8	0.048 (3)	0.060 (4)	0.040 (3)	-0.005 (3)	0.017 (3)	-0.013 (3)
N1	0.045 (3)	0.032 (2)	0.026 (2)	-0.0003 (18)	0.0029 (19)	0.0015 (16)
N2	0.027 (2)	0.0226 (18)	0.029 (2)	0.0039 (15)	-0.0020 (16)	-0.0014 (15)
O1	0.0329 (19)	0.0411 (19)	0.0284 (17)	0.0070 (15)	-0.0029 (15)	0.0076 (15)
O2	0.052 (2)	0.0301 (18)	0.042 (2)	-0.0086 (16)	0.0173 (17)	0.0011 (15)
O3	0.047 (2)	0.0254 (17)	0.048 (2)	0.0046 (15)	0.0133 (17)	0.0055 (15)
O4	0.041 (2)	0.058 (2)	0.0319 (19)	0.0148 (18)	-0.0095 (16)	-0.0110 (17)
O5	0.053 (2)	0.040 (2)	0.085 (3)	-0.0016 (19)	0.014 (2)	-0.010 (2)
O6	0.054 (3)	0.088 (3)	0.033 (2)	-0.016 (2)	0.0131 (19)	-0.014 (2)
O7	0.084 (3)	0.047 (2)	0.055 (3)	0.016 (2)	-0.007 (2)	-0.005 (2)
O8	0.063 (3)	0.113 (4)	0.045 (2)	-0.044 (3)	0.020 (2)	-0.022 (3)
Br1	0.0384 (3)	0.0382 (3)	0.0377 (3)	0.0004 (2)	0.0016 (2)	-0.0041 (2)
Br2	0.0453 (4)	0.0619 (4)	0.0406 (3)	-0.0004 (3)	0.0118 (3)	-0.0015 (3)
P1	0.0294 (6)	0.0237 (6)	0.0251 (6)	0.0022 (5)	0.0035 (5)	0.0006 (4)
P2	0.0386 (7)	0.0318 (7)	0.0308 (7)	-0.0040 (5)	0.0064 (6)	-0.0031 (5)

Geometric parameters (Å, °)

C1—N1	1.488 (7)	C7—C8	1.500 (8)
C1—C2	1.526 (8)	C7—N2	1.517 (6)
C1—H1A	0.9700	C7—H7A	0.9700
C1—H1B	0.9700	C7—H7B	0.9700
C2—N2	1.501 (6)	C8—Br2	1.945 (5)
C2—H2A	0.9700	C8—H8A	0.9700
C2—H2B	0.9700	C8—H8B	0.9700
C3—N1	1.501 (6)	N1—H1C	0.9100
C3—C4	1.510 (7)	O1—P1	1.549 (4)
C3—H3A	0.9700	O1—H1D	0.8200
C3—H3B	0.9700	O2—P1	1.507 (3)
C4—N2	1.511 (6)	O3—P1	1.505 (3)
C4—H4A	0.9700	O4—P1	1.556 (4)
C4—H4B	0.9700	O4—H4C	0.8200
C5—N1	1.486 (6)	O5—P2	1.550 (4)
C5—C6	1.519 (7)	O5—H5C	0.8200
C5—H5A	0.9700	O6—P2	1.468 (4)
C5—H5B	0.9700	O7—P2	1.554 (4)
C6—N2	1.509 (6)	O7—H7C	0.8200
C6—H6A	0.9700	O8—P2	1.539 (4)
C6—H6B	0.9700	O8—H8D	0.9600
N1—C1—C2	109.1 (4)	C8—C7—H7B	108.9
N1—C1—H1A	109.9	N2—C7—H7B	108.9
C2—C1—H1A	109.9	H7A—C7—H7B	107.7
N1—C1—H1B	109.9	C7—C8—Br2	107.2 (4)
C2—C1—H1B	109.9	C7—C8—H8A	110.3

H1A—C1—H1B	108.3	Br2—C8—H8A	110.3
N2—C2—C1	109.9 (4)	C7—C8—H8B	110.3
N2—C2—H2A	109.7	Br2—C8—H8B	110.3
C1—C2—H2A	109.7	H8A—C8—H8B	108.5
N2—C2—H2B	109.7	C5—N1—C1	109.8 (4)
C1—C2—H2B	109.7	C5—N1—C3	110.0 (4)
H2A—C2—H2B	108.2	C1—N1—C3	110.0 (4)
N1—C3—C4	109.3 (4)	C5—N1—H1C	109.0
N1—C3—H3A	109.8	C1—N1—H1C	109.0
C4—C3—H3A	109.8	C3—N1—H1C	109.0
N1—C3—H3B	109.8	C2—N2—C6	108.0 (4)
C4—C3—H3B	109.8	C2—N2—C4	108.8 (3)
H3A—C3—H3B	108.3	C6—N2—C4	109.3 (4)
C3—C4—N2	110.1 (4)	C2—N2—C7	112.3 (4)
C3—C4—H4A	109.6	C6—N2—C7	107.2 (4)
N2—C4—H4A	109.6	C4—N2—C7	111.1 (4)
C3—C4—H4B	109.6	P1—O1—H1D	109.5
N2—C4—H4B	109.6	P1—O4—H4C	109.5
H4A—C4—H4B	108.2	P2—O5—H5C	109.5
N1—C5—C6	109.0 (4)	P2—O7—H7C	109.5
N1—C5—H5A	109.9	P2—O8—H8D	109.0
C6—C5—H5A	109.9	O3—P1—O2	112.23 (19)
N1—C5—H5B	109.9	O3—P1—O1	110.5 (2)
C6—C5—H5B	109.9	O2—P1—O1	108.1 (2)
H5A—C5—H5B	108.3	O3—P1—O4	106.7 (2)
N2—C6—C5	110.2 (4)	O2—P1—O4	111.2 (2)
N2—C6—H6A	109.6	O1—P1—O4	108.1 (2)
C5—C6—H6A	109.6	O6—P2—O8	110.1 (3)
N2—C6—H6B	109.6	O6—P2—O5	113.7 (3)
C5—C6—H6B	109.6	O8—P2—O5	104.8 (3)
H6A—C6—H6B	108.1	O6—P2—O7	114.4 (3)
C8—C7—N2	113.5 (4)	O8—P2—O7	111.0 (3)
C8—C7—H7A	108.9	O5—P2—O7	102.3 (2)
N2—C7—H7A	108.9		
N1—C1—C2—N2	-3.1 (6)	C1—C2—N2—C4	61.1 (5)
N1—C3—C4—N2	-2.8 (6)	C1—C2—N2—C7	-175.5 (4)
N1—C5—C6—N2	-4.0 (6)	C5—C6—N2—C2	62.0 (5)
N2—C7—C8—Br2	178.6 (3)	C5—C6—N2—C4	-56.2 (5)
C6—C5—N1—C1	-58.3 (6)	C5—C6—N2—C7	-176.8 (4)
C6—C5—N1—C3	62.8 (6)	C3—C4—N2—C2	-57.6 (5)
C2—C1—N1—C5	62.7 (5)	C3—C4—N2—C6	60.1 (5)
C2—C1—N1—C3	-58.4 (5)	C3—C4—N2—C7	178.2 (4)
C4—C3—N1—C5	-59.0 (6)	C8—C7—N2—C2	-60.4 (6)
C4—C3—N1—C1	62.0 (6)	C8—C7—N2—C6	-178.9 (4)
C1—C2—N2—C6	-57.5 (5)	C8—C7—N2—C4	61.8 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1C \cdots O2	0.91	1.79	2.667 (6)	162
O1—H1D \cdots O6	0.82	1.71	2.519 (5)	170
O4—H4C \cdots O3 ⁱ	0.82	1.80	2.560 (5)	155
O5—H5C \cdots O3 ⁱ	0.82	1.73	2.555 (5)	179
O7—H7C \cdots O2 ⁱⁱ	0.82	1.77	2.555 (5)	159
O8—H8D \cdots Br1 ⁱⁱⁱ	0.96	2.18	3.100 (4)	160

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$; (ii) $-x+1, y-1/2, -z+3/2$; (iii) $x, y, z+1$.