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Structure Reports

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1,1,4,4-Tetramethylpiperazinediium dibromide

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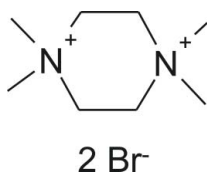
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
R factor = 0.025; wR factor = 0.061; data-to-parameter ratio = 14.4.

A small quantity of the title compound, $\text{C}_8\text{H}_{20}\text{N}_2^{2+} \cdot 2\text{Br}^-$, was formed as a by-product in a reaction between a diamine and an alkyl bromide. The asymmetric unit contains half of a centrosymmetric dication and a bromide anion. In the crystal, weak intermolecular $\text{C}-\text{H} \cdots \text{Br}$ hydrogen bonds consolidate the crystal packing.

Related literature

For a possible synthetic route, see Creighton & Taylor (1987). For related structures, see; Linden *et al.* (1999, 2002); Guo *et al.* (2007).



Experimental

Crystal data

 $\text{C}_8\text{H}_{20}\text{N}_2^{2+} \cdot 2\text{Br}^-$ $M_r = 304.08$ Monoclinic, $P2_1/c$ $a = 5.8769$ (12) Å $b = 8.4584$ (17) Å $c = 11.200$ (2) Å $\beta = 92.79$ (3)° $V = 556.07$ (19) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 7.25$ mm⁻¹ $T = 123$ K $0.24 \times 0.16 \times 0.16$ mm

Data collection

Bruker Kappa APEXII diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

 $T_{\min} = 0.296$, $T_{\max} = 0.390$

5032 measured reflections

1370 independent reflections

1223 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.061$ $S = 1.11$

1370 reflections

95 parameters

All H-atom parameters refined

 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.70$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C2}-\text{H2A} \cdots \text{Br1}^{\text{i}}$	0.96 (3)	2.88 (4)	3.816 (4)	165 (2)
$\text{C2}-\text{H2B} \cdots \text{Br1}$	0.93 (3)	2.92 (4)	3.820 (4)	163 (2)
$\text{C2}-\text{H2C} \cdots \text{Br1}^{\text{ii}}$	0.98 (3)	2.83 (4)	3.770 (3)	161 (2)
$\text{C3}-\text{H3B} \cdots \text{Br1}^{\text{iii}}$	1.00 (3)	2.84 (3)	3.806 (4)	163 (2)
$\text{C4}-\text{H4A} \cdots \text{Br1}^{\text{iv}}$	0.93 (3)	2.92 (2)	3.566 (2)	127 (2)
$\text{C4}-\text{H4B} \cdots \text{Br1}^{\text{ii}}$	0.97 (3)	2.86 (5)	3.787 (2)	159 (2)

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

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2642).

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supporting information

Acta Cryst. (2009). E65, o2952 [doi:10.1107/S1600536809045139]

1,1,4,4-Tetramethylpiperazinediium dibromide

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S1. Comment

Low quantity of the title compound (Fig. 1) was formed as a byproduct in a synthesis between a tetramethylethylenediamine (TMEDA) and ethoxyethylbromide. Most probably residues of dibromoethane existed as an impurity on either of the starting materials as it is known that piperazinium can be formed by reacting TMEDA and 1,2-dibromoethane. The compound has been recrystallized from acetonitrile/methanol solvent and its crystal structure is reported here.

The asymmetric unit consists of one anion and half a cation. The C—H···Br distances vary from 2.826 (30) to 2.924 (20) Å. In the crystal, cations are packed columnary along *a* axis forming at the same time layers along *b* axis. The bromide anions are analogously packed between the cation layers. The structure is stabilized by weak intermolecular C—H···Br interactions. Cation conformation of this compound is similar to those previously reported tetraiodidocadmate and pentabromothallate salts.

S2. Experimental

The compound was a byproduct from a reaction between tetramethylenediamine and ethoxyethylbromide. Few crystals suitable for a single-crystal structure determination recrystallized from an acetonitrile-methanol solution.

S3. Refinement

All H atoms were located from the difference map and refined isotropically.

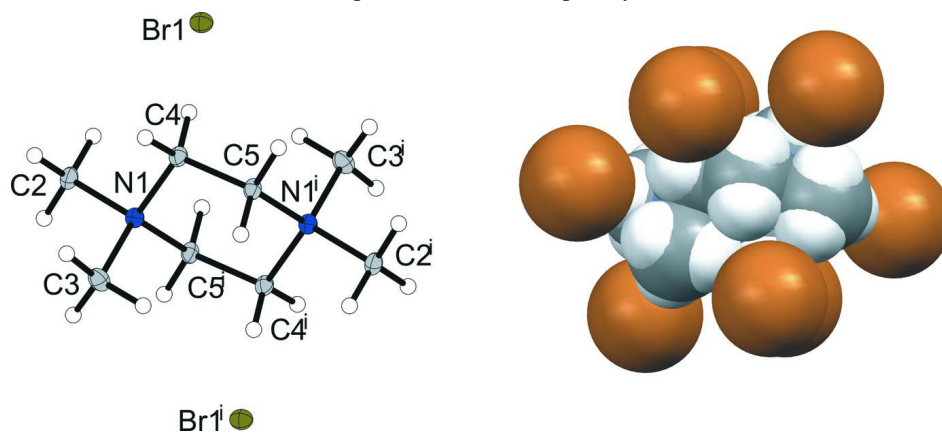


Figure 1

Left: The molecular structure of (I) showing 50% probability displacement ellipsoids and the atomic numbering [symmetry code: (i) $-x + 1, y + 1/2, -z + 3/2$]. Right: Spacefill presentation of location of eight bromides around a single cation. Six of the anions belong to the neighboring ion pairs.

1,1,4,4-Tetramethylpiperazinedium dibromide*Crystal data*

$C_8H_{20}N_2^{2+} \cdot 2Br^-$
 $M_r = 304.08$
 Monoclinic, $P2_1/c$
 $a = 5.8769$ (12) Å
 $b = 8.4584$ (17) Å
 $c = 11.200$ (2) Å
 $\beta = 92.79$ (3)°
 $V = 556.07$ (19) Å³
 $Z = 2$

$F(000) = 304$
 $D_x = 1.816$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3094 reflections
 $\theta = 0.4$ – 28.3 °
 $\mu = 7.25$ mm⁻¹
 $T = 123$ K
 Block, colourless
 $0.24 \times 0.16 \times 0.16$ mm

Data collection

Bruker Kappa APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.296$, $T_{\max} = 0.390$

5032 measured reflections
 1370 independent reflections
 1223 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 28.2$ °, $\theta_{\min} = 3.0$ °
 $h = -6 \rightarrow 7$
 $k = -11 \rightarrow 10$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.061$
 $S = 1.11$
 1370 reflections
 95 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.322P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.70$ e Å⁻³

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.5241 (3)	0.3260 (2)	0.48286 (16)	0.0111 (4)
C2	0.6413 (5)	0.1983 (3)	0.4148 (2)	0.0146 (5)
C3	0.3697 (5)	0.2474 (3)	0.5693 (2)	0.0155 (5)
C4	0.3920 (4)	0.4292 (3)	0.3948 (2)	0.0120 (4)
C5	0.2945 (4)	0.5749 (3)	0.4538 (2)	0.0117 (5)

Br1	0.89763 (4)	0.01387 (3)	0.702200 (19)	0.01391 (10)
H2A	0.524 (5)	0.137 (3)	0.374 (2)	0.017 (7)*
H2B	0.720 (5)	0.138 (3)	0.473 (2)	0.013 (7)*
H2C	0.733 (4)	0.252 (3)	0.356 (2)	0.011 (6)*
H3A	0.462 (5)	0.186 (3)	0.620 (2)	0.019 (7)*
H3B	0.292 (5)	0.333 (3)	0.614 (2)	0.020 (7)*
H3C	0.270 (5)	0.190 (3)	0.524 (3)	0.021 (8)*
H4A	0.272 (4)	0.370 (3)	0.360 (2)	0.010 (6)*
H4B	0.491 (5)	0.456 (3)	0.331 (2)	0.010 (6)*
H5A	0.182 (5)	0.546 (3)	0.519 (2)	0.013 (7)*
H5B	0.220 (4)	0.637 (3)	0.394 (2)	0.005 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0101 (10)	0.0108 (9)	0.0122 (9)	-0.0002 (7)	0.0004 (7)	-0.0004 (7)
C2	0.0186 (14)	0.0101 (11)	0.0149 (11)	0.0019 (10)	0.0000 (10)	-0.0024 (9)
C3	0.0157 (14)	0.0142 (12)	0.0168 (12)	-0.0011 (10)	0.0034 (10)	0.0033 (9)
C4	0.0128 (12)	0.0105 (10)	0.0122 (10)	0.0004 (9)	-0.0029 (9)	-0.0010 (9)
C5	0.0116 (12)	0.0095 (10)	0.0137 (11)	0.0019 (9)	-0.0034 (9)	-0.0011 (9)
Br1	0.01243 (16)	0.01658 (15)	0.01261 (14)	0.00082 (9)	-0.00030 (9)	-0.00037 (8)

Geometric parameters (Å, °)

N1—C4	1.505 (3)	C3—H3B	1.01 (3)
N1—C5 ⁱ	1.506 (3)	C3—H3C	0.90 (3)
N1—C2	1.507 (3)	C4—C5	1.524 (3)
N1—C3	1.512 (3)	C4—H4A	0.93 (3)
C2—H2A	0.96 (3)	C4—H4B	0.97 (3)
C2—H2B	0.93 (3)	C5—N1 ⁱ	1.506 (3)
C2—H2C	0.99 (3)	C5—H5A	1.04 (3)
C3—H3A	0.93 (3)	C5—H5B	0.94 (2)
C4—N1—C5 ⁱ	108.49 (18)	N1—C3—H3C	105.5 (18)
C4—N1—C2	108.52 (17)	H3A—C3—H3C	113 (2)
C5 ⁱ —N1—C2	107.85 (18)	H3B—C3—H3C	112 (2)
C4—N1—C3	111.58 (19)	N1—C4—C5	112.19 (18)
C5 ⁱ —N1—C3	112.09 (17)	N1—C4—H4A	108.5 (16)
C2—N1—C3	108.19 (18)	C5—C4—H4A	108.6 (16)
N1—C2—H2A	107.1 (16)	N1—C4—H4B	108.0 (16)
N1—C2—H2B	105.1 (16)	C5—C4—H4B	112.5 (15)
H2A—C2—H2B	111 (2)	H4A—C4—H4B	107 (2)
N1—C2—H2C	106.7 (15)	N1 ⁱ —C5—C4	112.47 (19)
H2A—C2—H2C	109 (2)	N1 ⁱ —C5—H5A	104.9 (15)
H2B—C2—H2C	117 (2)	C4—C5—H5A	112.6 (15)
N1—C3—H3A	106.8 (18)	N1 ⁱ —C5—H5B	108.7 (15)
N1—C3—H3B	107.6 (15)	C4—C5—H5B	108.2 (14)
H3A—C3—H3B	112 (2)	H5A—C5—H5B	110 (2)

C5 ⁱ —N1—C4—C5	-55.1 (3)	C3—N1—C4—C5	68.8 (2)
C2—N1—C4—C5	-172.1 (2)	N1—C4—C5—N1 ⁱ	57.4 (3)

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

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>
C2—H2A \cdots Br1 ⁱⁱ	0.96 (3)	2.88 (4)	3.816 (4)	165 (2)
C2—H2B \cdots Br1	0.93 (3)	2.92 (4)	3.820 (4)	163 (2)
C2—H2C \cdots Br1 ⁱⁱⁱ	0.98 (3)	2.83 (4)	3.770 (3)	161 (2)
C3—H3B \cdots Br1 ^{iv}	1.00 (3)	2.84 (3)	3.806 (4)	163 (2)
C4—H4A \cdots Br1 ^v	0.93 (3)	2.92 (2)	3.566 (2)	127 (2)
C4—H4B \cdots Br1 ⁱⁱⁱ	0.97 (3)	2.86 (5)	3.787 (2)	159 (2)

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