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4-(Dimethylamino)pyridinium tribromide: whole molecule disorder of cation and anion

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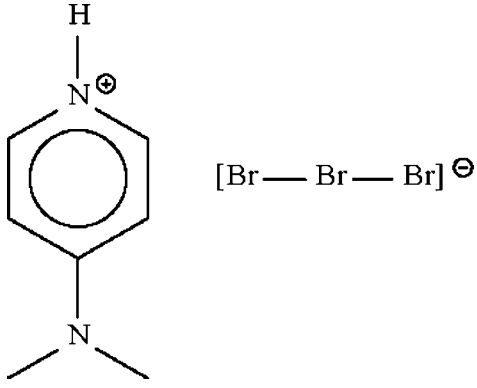
Key indicators: single-crystal X-ray study; T = 100 K; mean σ() = 0.000 Å; disorder in main residue; R factor = 0.021; wR factor = 0.051; data-to-parameter ratio = 12.6.

In the title salt, $C_7H_{11}N_2^+\cdot Br_3^-$, the cation and the near-linear anion [Br—Br—Br = 179.41 (8)°] both show whole-molecule disorder about crystallographic twofold rotation axes. The cation is weakly hydrogen-bonded to the anion by an N—H···Br interaction. The crystal studied was found to be a racemic twin, with a twin component of nearly 50%.

Related literature

The compound is known commercially as 4-(dimethylamino)-pyridine hydrobromide perbromide, $[C_7H_{10}N_2]\cdot[HBr]\cdot[Br_2]$. The 4-dimethylaminopyridinium cation furnishes a number of salts with organic and inorganic acids. For 4-dimethylamino-pyridinium bromide, see: Mayr-Stein & Bolte (2000). For dimethylaminopyridinium chloride and its dihydrate, see: Bryant & King (1992); Chao *et al.* (1977).



Experimental

Crystal data

$C_7H_{11}N_2^+\cdot Br_3^-$
M_r = 362.91
Orthorhombic, $P222_1$
a = 4.1688 (1) Å
b = 8.8349 (2) Å
c = 14.7255 (4) Å
V = 542.35 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 11.11 mm^{-1}
T = 100 K
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.656, T_{max} = 1.000
(expected range = 0.216–0.329)
5156 measured reflections
1256 independent reflections
1114 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.051
S = 0.98
1256 reflections
100 parameters
60 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Absolute structure: Flack (1983), 480 Friedel pairs
Flack parameter: 0.47 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Br2	0.88	2.42	3.286 (2)	167

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); 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, 2009).

I thank the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2966).

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supporting information

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4-(Dimethylamino)pyridinium tribromide: whole molecule disorder of cation and anion

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S1. Experimental

Commercially-available 4-dimethylaminopyridine hydrobromide perbromide was recrystallized from ethanol to give colourless blocks of (I).

S2. Refinement

The Br_3 anion lies on a twofold rotation axis, but it was allowed to refine off this symmetry element as a three-atom species.

The cation is disordered about another twofold rotation axis; this was refined as a cation with its atoms of half occupancies. The pyridyl portion was refined as a rigid hexagon of 1.39 Å sides; the pair of N–C_{methyl} distances were restrained to within 0.01 Å of each other. The cation was restrained to be nearly planar, and the anisotropic displacement factors were restrained to be nearly isotropic.

The hydrogen atoms were placed at calculated positions (C–H 0.95, N–H 0.88 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C,*N*).

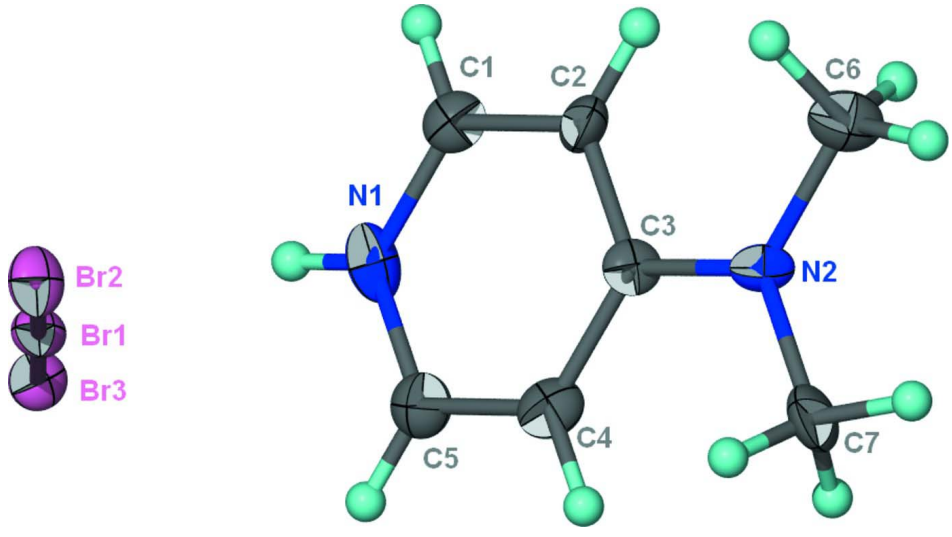

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $[C_7H_{11}N_2][Br_3]$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius.

4-(Dimethylamino)pyridinium tribromide

Crystal data

$C_7H_{11}N_2^+\cdot Br_3^-$
$M_r = 362.91$
Orthorhombic, $P222_1$
Hall symbol: P 2c 2
$a = 4.1688$ (1) Å
$b = 8.8349$ (2) Å
$c = 14.7255$ (4) Å
$V = 542.35$ (2) Å^3
$Z = 2$
$F(000) = 344$
$D_x = 2.222$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2094 reflections
$\theta = 2.7$–$28.3°$
$\mu = 11.11$ mm^{-1}
$T = 100$ K
Block, colorless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.656$, $T_{max} = 1.000$
5156 measured reflections
1256 independent reflections
1114 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$h = -5\rightarrow5$
$k = -11\rightarrow11$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.051$
$S = 0.98$
1256 reflections
100 parameters
60 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
$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack (1983), 480 Friedel pairs
Absolute structure parameter: 0.47 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.5290 (6)	0.25953 (5)	0.23869 (12)	0.0155 (3)	0.50
Br2	0.2738 (3)	0.27497 (11)	0.07779 (5)	0.0196 (2)	0.50
Br3	0.7682 (3)	0.24565 (11)	0.39355 (5)	0.01777 (18)	0.50
N2	1.1882 (7)	0.2417 (5)	−0.3550 (3)	0.0144 (9)	0.50
N1	0.7232 (7)	0.2399 (4)	−0.10428 (15)	0.0209 (11)	0.50
H1	0.6250	0.2392	−0.0514	0.025*	0.50
C1	0.7724 (9)	0.1050 (3)	−0.1509 (2)	0.0190 (11)	0.50

H1A	0.7000	0.0122	−0.1257	0.023*	0.50
C2	0.9276 (8)	0.1061 (3)	−0.23446 (19)	0.0196 (13)	0.50
H2	0.9612	0.0140	−0.2663	0.024*	0.50
C3	1.0335 (5)	0.2420 (3)	−0.27138 (13)	0.0147 (11)	0.50
C4	0.9844 (9)	0.3768 (3)	−0.2248 (2)	0.0195 (12)	0.50
H4	1.0568	0.4697	−0.2500	0.023*	0.50
C5	0.8292 (9)	0.3757 (3)	−0.1412 (2)	0.0208 (14)	0.50
H5	0.7956	0.4679	−0.1093	0.025*	0.50
C6	1.2376 (13)	0.1015 (6)	−0.4024 (3)	0.0226 (13)	0.50
H6A	1.0314	0.0498	−0.4102	0.034*	0.50
H6B	1.3829	0.0370	−0.3672	0.034*	0.50
H6C	1.3321	0.1220	−0.4620	0.034*	0.50
C7	1.2983 (11)	0.3839 (6)	−0.3936 (4)	0.0223 (14)	0.50
H7A	1.1130	0.4479	−0.4077	0.033*	0.50
H7B	1.4196	0.3638	−0.4493	0.033*	0.50
H7C	1.4366	0.4359	−0.3497	0.033*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0195 (8)	0.01421 (16)	0.0128 (8)	−0.0005 (3)	0.0021 (5)	−0.0007 (2)
Br2	0.0201 (4)	0.0274 (5)	0.0112 (4)	0.0019 (3)	0.0015 (3)	−0.0010 (3)
Br3	0.0210 (4)	0.0207 (4)	0.0116 (4)	−0.0011 (3)	0.0007 (3)	0.0001 (3)
N2	0.021 (2)	0.0110 (19)	0.011 (2)	−0.001 (2)	−0.0034 (17)	0.005 (2)
N1	0.023 (3)	0.032 (3)	0.008 (2)	0.007 (3)	0.0025 (19)	−0.001 (2)
C1	0.019 (3)	0.021 (3)	0.017 (3)	−0.001 (2)	−0.003 (3)	0.002 (2)
C2	0.012 (3)	0.0175 (19)	0.029 (4)	−0.0005 (16)	0.004 (3)	0.003 (2)
C3	0.019 (2)	0.0179 (18)	0.008 (3)	−0.001 (3)	−0.002 (2)	0.0001 (17)
C4	0.020 (2)	0.022 (2)	0.016 (3)	−0.004 (3)	−0.005 (4)	0.0004 (16)
C5	0.019 (3)	0.023 (3)	0.020 (3)	0.001 (2)	−0.001 (3)	0.001 (3)
C6	0.032 (3)	0.019 (2)	0.017 (3)	0.000 (3)	−0.001 (4)	0.004 (2)
C7	0.023 (4)	0.023 (3)	0.020 (3)	0.005 (2)	0.008 (3)	−0.005 (2)

Geometric parameters (Å, º)

Br1—Br3	2.492 (3)	C2—H2	0.9500
Br1—Br2	2.601 (3)	C3—C4	1.3900
N2—C3	1.390 (5)	C4—C5	1.3900
N2—C6	1.436 (7)	C4—H4	0.9500
N2—C7	1.454 (7)	C5—H5	0.9500
N1—C1	1.3900	C6—H6A	0.9800
N1—C5	1.3900	C6—H6B	0.9800
N1—H1	0.8800	C6—H6C	0.9800
C1—C2	1.3900	C7—H7A	0.9800
C1—H1A	0.9500	C7—H7B	0.9800
C2—C3	1.3900	C7—H7C	0.9800
Br3—Br1—Br2	179.41 (8)	C5—C4—H4	120.0

C3—N2—C6	119.9 (4)	C3—C4—H4	120.0
C3—N2—C7	119.4 (4)	C4—C5—N1	120.0
C6—N2—C7	120.7 (4)	C4—C5—H5	120.0
C1—N1—C5	120.0	N1—C5—H5	120.0
C1—N1—H1	120.0	N2—C6—H6A	109.5
C5—N1—H1	120.0	N2—C6—H6B	109.5
N1—C1—C2	120.0	H6A—C6—H6B	109.5
N1—C1—H1A	120.0	N2—C6—H6C	109.5
C2—C1—H1A	120.0	H6A—C6—H6C	109.5
C1—C2—C3	120.0	H6B—C6—H6C	109.5
C1—C2—H2	120.0	N2—C7—H7A	109.5
C3—C2—H2	120.0	N2—C7—H7B	109.5
N2—C3—C4	120.5 (3)	H7A—C7—H7B	109.5
N2—C3—C2	119.5 (3)	N2—C7—H7C	109.5
C4—C3—C2	120.0	H7A—C7—H7C	109.5
C5—C4—C3	120.0	H7B—C7—H7C	109.5

C5—N1—C1—C2	0.0	C1—C2—C3—N2	−179.96 (9)
N1—C1—C2—C3	0.0	C1—C2—C3—C4	0.0
C6—N2—C3—C4	179.95 (9)	N2—C3—C4—C5	179.96 (9)
C7—N2—C3—C4	−0.07 (11)	C2—C3—C4—C5	0.0
C6—N2—C3—C2	−0.08 (13)	C3—C4—C5—N1	0.0
C7—N2—C3—C2	179.90 (9)	C1—N1—C5—C4	0.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br2	0.88	2.42	3.286 (2)	167