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# Redetermination of 4-(dimethylamino)-pyridinium tribromide

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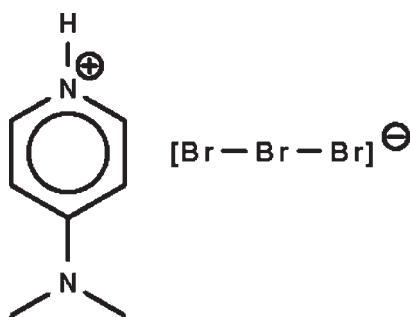
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.040; data-to-parameter ratio = 21.6.

In the title salt,  $\text{C}_7\text{H}_{11}\text{N}_2^+\cdot\text{Br}_3^-$ , the essentially planar cation (r.m.s. deviation = 0.006 Å) forms an  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bond to one of the Br atoms of the almost linear anion [ $\text{Br}-\text{Br}-\text{Br} = 179.31(2)^\circ$ ]. The crystal studied was found to be a racemic twin. The whole-molecule disorder of the cation and anion about a twofold rotation axis described earlier [Ng (2009). *Acta Cryst.* **E65**, o1276] is an artifact of halving one of the axes of the orthorhombic unit cell.

## Related literature

For the refinement based on a unit cell half as large, see: Ng (2009).



## Experimental

### Crystal data

 $\text{C}_7\text{H}_{11}\text{N}_2^+\cdot\text{Br}_3^-$ 
 $M_r = 362.91$ 

 Orthorhombic,  $P2_12_12$   
 $a = 14.7253(2)$  Å  
 $b = 17.6696(3)$  Å  
 $c = 4.1689(1)$  Å  
 $V = 1084.71(4)$  Å<sup>3</sup>
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 11.11$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.20 \times 0.15 \times 0.10$  mm

### Data collection

 Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.215$ ,  $T_{\max} = 0.403$ 

 10364 measured reflections  
 2502 independent reflections  
 2300 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.040$   
 $S = 0.98$   
 2502 reflections  
 116 parameters  
 H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 999 Friedel pairs  
 Flack parameter: 0.51 (2)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{Br1}$	0.92 (3)	2.41 (3)	3.323 (2)	171 (3)

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE*; 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: *pubCIF* (Westrip, 2010).

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: HB5583).

## References

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# supporting information

*Acta Cryst.* (2010). E66, o2223 [https://doi.org/10.1107/S1600536810030369]

## Redetermination of 4-(dimethylamino)pyridinium tribromide

Seik Weng Ng

### S1. Comment

Dimethylaminopyridinium tribromide (I) was refined as a whole-molecule-disordered cation and anion that was disordered about a crystallographic twofold rotation axis (Ng, 2009) in the orthorhombic  $P222_1$  space group [unit cell parameters 4.1688 (1), 8.8349 (2), 14.7255 (4) Å]. The automatic cell-searching program had, in fact, missed some weaker reflections, so that the true  $b$ -axis should be doubled, so that the space group would be  $P22_12_1$  [4.1689 (1), 17.6696 (3), 14.7253 (2) Å]. In the standard  $P2_12_12$  setting, the structure refines smoothly, without disorder, to a final  $R$  index of 0.019 (Fig. 1). The disorder is an artifact of halving one of the axis, and a chemically reasonable model coincidentally arose owing to the nature of both the planar cation and linear anion.

### S2. Experimental

The diffraction measurements were those used in the previous study (Ng, 2009). Measurements on another different specimen gave the same refinement results, especially with respect to the 0.5 Flack parameter.

### S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 Å for the aromatic H-atoms and 0.98 Å for the methyl H-atoms) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to 1.2 to 1.5 $U(\text{C})$ .

The ammonium H-atom was located in a difference Fourier map, and was refined without a restraint.

The structure is a racemic twin; the Flack parameter was refined on 999 Friedel pairs.

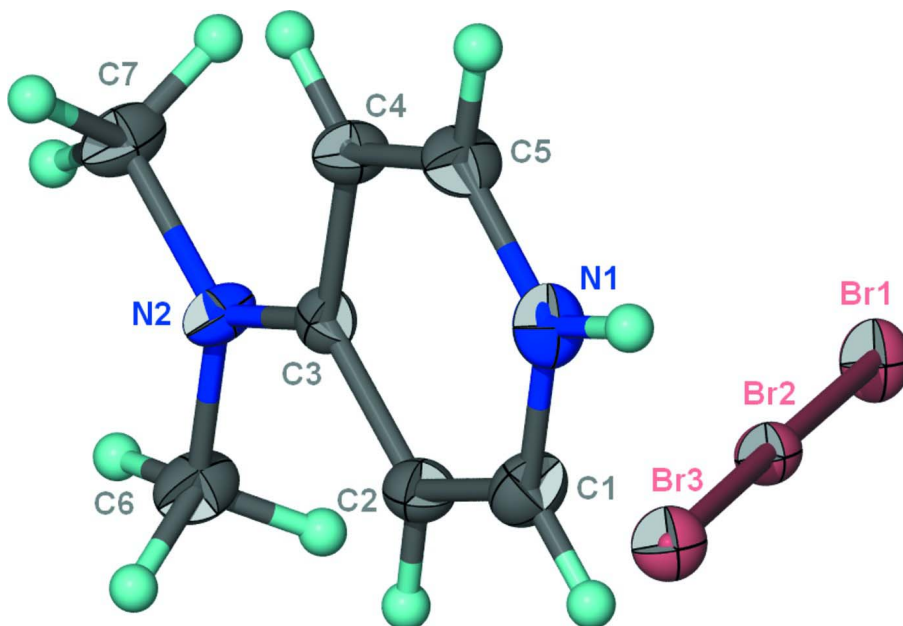


Figure 1

The molecular structure of (I) 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,  $P2_12_12$

Hall symbol: P 2 2ab

$a = 14.7253 (2) \text{ \AA}$

$b = 17.6696 (3) \text{ \AA}$

$c = 4.1689 (1) \text{ \AA}$

$V = 1084.71 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 688$

$D_x = 2.222 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4074 reflections

$\theta = 2.7\text{--}28.3^\circ$

$\mu = 11.11 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colorless

$0.20 \times 0.15 \times 0.10 \text{ mm}$

##### Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.215$ ,  $T_{\max} = 0.403$

10364 measured reflections

2502 independent reflections

2300 reflections with  $I > 2\sigma(I)$

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

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.8^\circ$

$h = -19 \rightarrow 19$

$k = -22 \rightarrow 22$

$l = -5 \rightarrow 5$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.040$

$S = 0.98$

2502 reflections

116 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 atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 999 Friedel  
pairs

Absolute structure parameter: 0.51 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.422049 (17)	0.112471 (15)	0.72575 (7)	0.01934 (7)
Br2	0.261320 (17)	0.120225 (14)	0.47003 (7)	0.01501 (7)
Br3	0.106438 (17)	0.127359 (14)	0.23133 (7)	0.01826 (7)
N1	0.60669 (15)	0.13040 (13)	0.2738 (6)	0.0196 (5)
H1	0.553 (2)	0.1299 (18)	0.387 (8)	0.038 (10)*
N2	0.85347 (15)	0.12901 (12)	-0.1849 (6)	0.0162 (5)
C1	0.6420 (2)	0.06411 (16)	0.1723 (7)	0.0218 (7)
H1A	0.6095	0.0185	0.2093	0.026*
C2	0.72305 (19)	0.06148 (15)	0.0185 (7)	0.0182 (6)
H2	0.7468	0.0143	-0.0520	0.022*
C3	0.77231 (17)	0.12906 (14)	-0.0370 (6)	0.0148 (5)
C4	0.73201 (19)	0.19758 (15)	0.0729 (7)	0.0179 (6)
H4	0.7621	0.2445	0.0396	0.021*
C5	0.65084 (18)	0.19580 (14)	0.2248 (8)	0.0200 (6)
H5	0.6246	0.2418	0.2982	0.024*
C6	0.89406 (19)	0.05789 (14)	-0.2953 (8)	0.0221 (7)
H6A	0.9021	0.0237	-0.1124	0.033*
H6B	0.9532	0.0683	-0.3936	0.033*
H6C	0.8540	0.0341	-0.4538	0.033*
C7	0.90234 (17)	0.19907 (14)	-0.2435 (9)	0.0215 (6)
H7A	0.8653	0.2324	-0.3782	0.032*
H7B	0.9597	0.1879	-0.3532	0.032*
H7C	0.9150	0.2242	-0.0387	0.032*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01273 (13)	0.02577 (14)	0.01951 (15)	-0.00074 (11)	0.00148 (13)	0.00173 (13)
Br2	0.01278 (13)	0.01445 (12)	0.01779 (13)	-0.00072 (11)	0.00346 (11)	-0.00043 (11)
Br3	0.01313 (13)	0.02064 (13)	0.02101 (14)	-0.00046 (11)	0.00112 (13)	-0.00002 (14)
N1	0.0121 (11)	0.0263 (12)	0.0204 (13)	0.0014 (10)	0.0026 (12)	0.0015 (13)
N2	0.0133 (11)	0.0125 (10)	0.0228 (13)	0.0005 (9)	0.0026 (10)	0.0024 (10)
C1	0.0188 (16)	0.0211 (15)	0.0255 (18)	-0.0030 (13)	0.0007 (14)	0.0025 (12)
C2	0.0195 (15)	0.0157 (13)	0.0196 (16)	0.0012 (11)	0.0001 (15)	-0.0015 (12)
C3	0.0135 (13)	0.0170 (12)	0.0140 (12)	0.0004 (12)	-0.0034 (12)	0.0014 (12)
C4	0.0154 (14)	0.0157 (13)	0.0225 (16)	-0.0005 (12)	0.0018 (14)	-0.0014 (11)
C5	0.0177 (14)	0.0186 (13)	0.0236 (17)	0.0051 (11)	0.0038 (17)	-0.0030 (14)
C6	0.0183 (15)	0.0178 (13)	0.0303 (19)	0.0030 (12)	0.0047 (18)	0.0008 (14)
C7	0.0141 (14)	0.0179 (13)	0.0323 (18)	-0.0011 (11)	0.0072 (18)	0.0024 (15)

*Geometric parameters (Å, °)*

Br1—Br2	2.5994 (4)	C2—H2	0.9500
Br2—Br3	2.4915 (4)	C3—C4	1.424 (4)
N1—C5	1.342 (3)	C4—C5	1.353 (4)
N1—C1	1.350 (4)	C4—H4	0.9500
N1—H1	0.92 (3)	C5—H5	0.9500
N2—C3	1.345 (3)	C6—H6A	0.9800
N2—C7	1.453 (3)	C6—H6B	0.9800
N2—C6	1.466 (3)	C6—H6C	0.9800
C1—C2	1.356 (4)	C7—H7A	0.9800
C1—H1A	0.9500	C7—H7B	0.9800
C2—C3	1.416 (4)	C7—H7C	0.9800
Br3—Br2—Br1	179.314 (16)	C5—C4—H4	120.0
C5—N1—C1	120.9 (2)	C3—C4—H4	120.0
C5—N1—H1	120 (2)	N1—C5—C4	121.3 (3)
C1—N1—H1	119 (2)	N1—C5—H5	119.4
C3—N2—C7	121.1 (2)	C4—C5—H5	119.4
C3—N2—C6	120.5 (2)	N2—C6—H6A	109.5
C7—N2—C6	118.4 (2)	N2—C6—H6B	109.5
N1—C1—C2	121.2 (3)	H6A—C6—H6B	109.5
N1—C1—H1A	119.4	N2—C6—H6C	109.5
C2—C1—H1A	119.4	H6A—C6—H6C	109.5
C1—C2—C3	119.9 (3)	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—C2	122.0 (2)	H7A—C7—H7B	109.5
N2—C3—C4	121.2 (2)	N2—C7—H7C	109.5
C2—C3—C4	116.8 (2)	H7A—C7—H7C	109.5
C5—C4—C3	119.9 (3)	H7B—C7—H7C	109.5
C5—N1—C1—C2	0.1 (5)	C1—C2—C3—N2	179.1 (3)
N1—C1—C2—C3	0.2 (4)	C1—C2—C3—C4	-0.6 (4)
C7—N2—C3—C2	179.1 (3)	N2—C3—C4—C5	-179.1 (3)
C6—N2—C3—C2	0.1 (4)	C2—C3—C4—C5	0.6 (4)
C7—N2—C3—C4	-1.2 (4)	C1—N1—C5—C4	-0.1 (5)
C6—N2—C3—C4	179.8 (3)	C3—C4—C5—N1	-0.3 (5)

*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—H1 $\cdots$ Br1	0.92 (3)	2.41 (3)	3.323 (2)	171 (3)