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3-Cyano-*N*-methylpyridinium bromide

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.063
Data-to-parameter ratio = 101.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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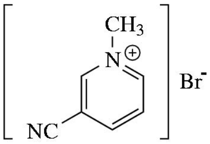
The title compound, $C_7H_7N_2^+\cdot Br^-$, forms a layered solid with each cation forming three strong and one weaker C—H···Br hydrogen bonds within the layer. All atoms except two of the methyl H atoms lie on a mirror plane.

Comment

Like 3-cyano-*N*-methylpyridinium chloride (Koplitz *et al.*, 2003), the isostructural bromide salt, (I), has crystallographic mirror symmetry. It features four C—H···Br interactions which can be characterized as hydrogen bonds (Table 1). Specifically, those C···Br distances involving atoms C2, C4 and C6 are all shorter than the average of 3.75 (2) Å given by Steiner (1998) for C—H···Br^- hydrogen bonds, while that involving atom C1 is not much longer. In Table 1, the column headed H···Br gives the experimental H···Br distances based on calculated H-atom positions with C—H = 0.95 Å, while the values in brackets are those determined using C—H distances of 1.083 Å [common practice to correct for the 'shortening' of the C—H distance in the X-ray experiment (Brammer *et al.*, 2001; Steiner, 1998; Lommerse *et al.*, 1996; Allen, 1986)]. Here, the corrected values for the H···Br contacts involving atoms H2, H4 and H6 are well below Steiner's average value of 2.64 (1) Å, suggesting that these are robust interactions. The corrected H1*A*···Br distance is rather long compared to Steiner's value but is still shorter than a normal van der Waals contact (*ca* 3.06 Å). The C—H···Br angles determined from the corrected H-atom positions differ from the experimental values by no more than 1° and are well within the range accepted for C—H···*X* hydrogen bonds. In addition, the corrected H5···N2 distance of 2.47 Å is only slightly longer than for the corresponding separation in the chloride salt (Koplitz *et al.*, 2003), indicating this to be also an attractive interaction. Consistent with the presence of these moderately strong intermolecular interactions, the title compound does not readily melt, but rather decomposes with charring at 493 K.



(I)

Experimental

An aqueous solution of 3-cyano-*N*-methylpyridinium iodide (Koplitz *et al.*, 2003) was passed down a column of polymer-supported bromide ion exchange resin (Aldrich catalogue No. 51,376–8) and the eluate evaporated to dryness. Crystals for the structure determination were grown by slow evaporation of a solution of the compound in a 1:1 (*v*/*v*) mixture of acetonitrile and ethanol. Analysis calculated for $C_7H_7N_2Br$: C 42.23, H 3.55, N 14.08, Br 40.14%; found: C 41.9, H 3.9, N 14.0, Br 39.3%. IR absorption bands (KBr pellet): C—H stretch, 3083 (*m*), 2999 (*s*), 2954 (*s*), 2926 (*s*), 2849 (*m*) cm^{-1}; C—N stretch: 2244 (*m*) cm^{-1}; C—H in-plane deformation: 1639 (*m*), 1507 (*m*) cm^{-1}. C—H out-of-plane deformation: 834 (*m*), 671 (*s*) cm^{-1}. ^{1}H NMR chemical shifts (D_2O): δ 9.40 (*s*, 1H, H2), 9.06 (*d*, 1H, H4), 8.89 (*d*, 1H, H6), 8.21 (*t*, 1H, H5), 4.44 (*s*, 3H, H1*A*,*B*).

Crystal data

$C_7H_7N_2^+\cdot Br^-$
$M_r = 199.06$
Monoclinic, $P2_1/m$
$a = 8.109$ (1) Å
$b = 6.6266$ (8) Å
$c = 8.381$ (1) Å
$\beta = 113.406$ (2)°
$V = 413.30$ (9) Å^3
$Z = 2$

$D_x = 1.600$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 4284 reflections
$\theta = 2.7$–28.2°
$\mu = 4.90$ mm^{-1}
$T = 100$ (2) K
Plate, colorless
0.16 × 0.11 × 0.01 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2003)
$T_{min} = 0.515$, $T_{max} = 0.948$
6277 measured reflections

6277 independent reflections
5502 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.7°$
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.063$
$S = 0.93$
6277 reflections
62 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.15$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Close-contact parameters for (I) (Å,°), with corrected values in parentheses.

	$H\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1*A*···Br	2.98 [2.85]	3.907 (1)	164 [165]
C2—H2···Br^{i}	2.58 [2.44]	3.528 (1)	179 [180]
C4—H4···Br^{ii}	2.64 [2.51]	3.585 (1)	172 [172]
C6—H6···Br	2.65 [2.52]	3.582 (1)	166 [166[
C5—H5···N2^{iii}	2.59 [2.47]	3.479 (2)	154 [155]

Symmetry codes: (i) 1 + *x*, *y*, *z*. (ii) 1 + *x*, *y*, 1+*z*. (iii) *x* − 1, *y*, *z*.

Using 746 reflections chosen from the full data set, it was determined that the crystal was twinned by a rotation of 180° about the real axis [001] (*CELL_NOW*; Sheldrick, 2004). Using the orientation matrices produced by this program, the data were reduced to F^2 values using the two-component version of *SAINT-Plus* (Bruker, 2004). In the final refinement, the two-component reflection file was used with no averaging of equivalent reflections (including Friedel opposites). H atoms were placed in calculated positions (C—H = 0.95 Å) and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the the attached C atoms. The maximum electron-density peak is 0.02 Å from the Br atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

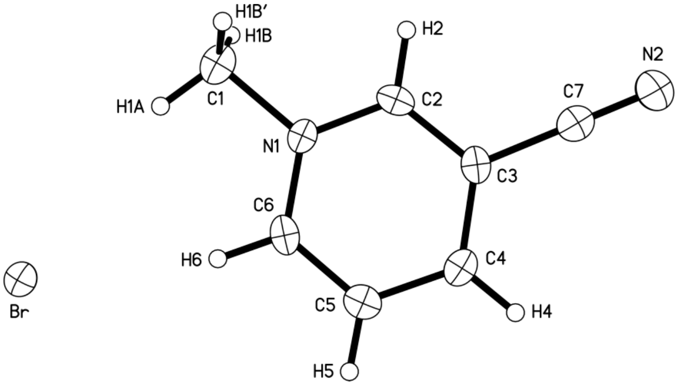


Figure 1
The title compound, viewed down the *b* axis. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.

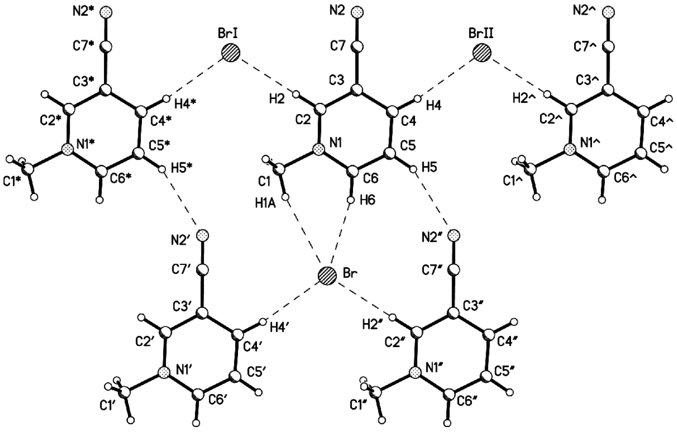


Figure 2
A portion of a layer of (I), showing the hydrogen bonding (dashed lines). [Symmetry codes: (I) 1 + *x*, *y*, *z*; (II) 1 + *x*, *y*, 1 + *z*; (*) *x*, *y*, −1 + *z*; (′) −1 + *x*, *y*, −1 + *z*; (″) −1 + *x*, *y*, *z*; (^) *x*, *y*, 1 + *z*.]

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