(4-Methylphenyl)methanaminium bromide hemi-hydrate

R Aarthi,[a] A Thiruvalluvar[b]* and C Ramachandra Raja[a]

[a]Department of Physics, Government Arts College (Autonomous), Kumbakonam 612 002, Tamilnadu, India, and [b]Kunthavai Naacchiyaar Government Arts College for Women (Autonomous), Thanjavur 613 007, Tamilnadu, India. *Correspondence e-mail: thiruvalluvar.a@gmail.com

In the title hydrated salt, $C_8H_{12}N^+\cdot Br^-\cdot 0.5H_2O$, which is isostructural with its chloride congener, the water O atom lies on a crystallographic twofold axis. In the crystal, the components are linked *via* C—H$\cdots$Br, O—H$\cdots$Br, N—H$\cdots$Br and N—H$\cdots$O hydrogen bonds to generate (100) sheets. The sheets are linked by two weak C—H$\cdots\pi$ interactions, generating a three-dimensional network.

3D view
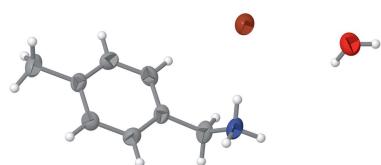
Chemical scheme
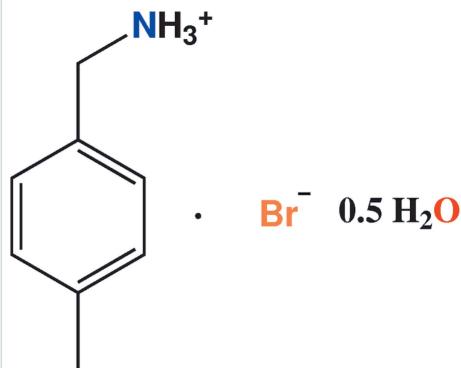
Structure description

Some noncentrosymmetric organic crystals exhibit high nonlinear efficiency and can be functionalized very easily but it is difficult to grow bulk crystals and their physical and mechanical properties are poor (Dolbecq *et al.*, 2010). As part of our ongoing studies in this area (Aarthi *et al.*, 2017), we now describe the synthesis and structure of (4-methylphenyl)methanaminium bromide hemihydrate, (I) (Fig. 1), which crystallized in a centrosymmetric space group.

The water O atom lies on a crystallographic twofold axis. In the crystal, the components are linked *via* C8—H8*B*$\cdots$Br1[i], O1—H1$\cdots$Br1[i], N1—H1*D*$\cdots$Br1, N1—H1*E*$\cdots$O1[ii], N1—H1*F*$\cdots$Br1[i] and N1—H1*F*$\cdots$Br1[ii] hydrogen bonds (see Fig. 2 and Table 1), generating layers lying parallel to the *bc* plane. Furthermore, the crystal structure features weak C1—H1*A*$\cdots\pi$[iii] and C8—H8*A*$\cdots\pi$[i] interactions, forming a three-dimensional network (see Fig. 3 and Table 1).

Souissi *et al.* (2010) have reported the related crystal structure of (4-chlorophenyl)methanaminium chloride hemihydrate.

Synthesis and crystallization

An aqueous solution containing 2 mmol of HBr in 20 ml of water was added to 2 mmol of 4-methylbenzylamine in 20 ml of water. The resultant solution was well stirred using a

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

$Cg1$ is the centroid of the C2–C7 benzene ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Br1^i	0.85 (2)	2.45 (2)	3.2870 (17)	169 (3)
N1—H1$D\cdots$Br1	0.92 (2)	2.40 (2)	3.314 (2)	178 (2)
N1—H1$E\cdots$O1^{ii}	0.90 (2)	2.05 (2)	2.883 (3)	155 (2)
N1—H1$F\cdots$Br1^i	0.91 (2)	2.89 (2)	3.554 (2)	131 (2)
N1—H1$F\cdots$Br1^{ii}	0.91 (2)	2.74 (3)	3.4383 (17)	134 (2)
C8—H8$B\cdots$Br1^i	0.97	3.05	3.670 (2)	123
C1—H1$A\cdots Cg1^{iii}$	0.96	2.73	3.634 (2)	157
C8—H8$A\cdots Cg1^i$	0.97	2.90	3.530 (2)	123

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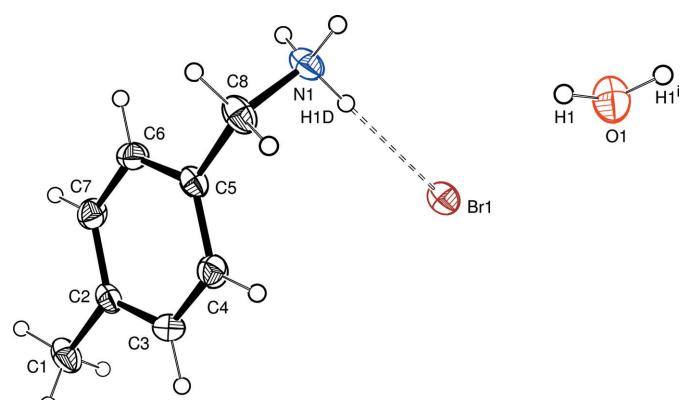

Figure 1
A view of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. [Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{12}N^+ \cdot Br^- \cdot 0.5H_2O$
M_r	211.11
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	293
a, b, c (Å)	30.7456 (18), 5.0266 (3), 12.0636 (7)
β (°)	98.430 (2)
V (Å^3)	1844.24 (19)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.40
Crystal size (mm)	$0.10 \times 0.10 \times 0.05$
Data collection	
Diffractometer	Bruker KappaCCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.534, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11261, 2479, 2129
R_{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.067, 1.06
No. of reflections	2479
No. of parameters	113
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.51

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015a), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009), *SHELXL2018* (Sheldrick, 2015b) and *publCIF* (Westrip, 2010).

Figure 2
The crystal structure of (I), viewed down the b axis, showing the formation of hydrogen bonding. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.
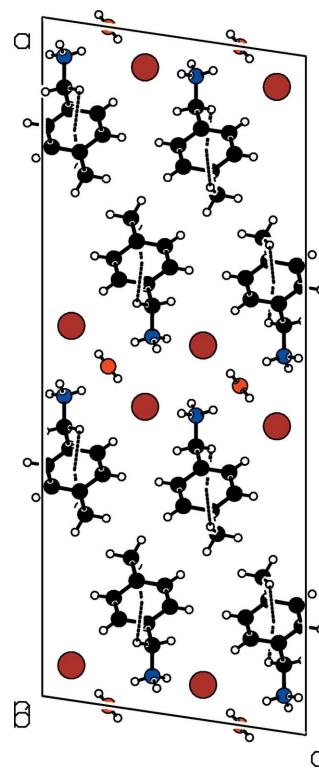

Figure 3
A partial packing diagram of (I), viewed down the b axis, showing the C—H$\cdots\pi$ interactions.

magnetic stirrer for 3 h and left to stand at room temperature. After 15 d, colourless blocks of (I) were harvested.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The O– and N-bonded H atoms were refined with restraints and the C-bound H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (aromatic), 0.97 (–CH$_2$–) and 0.96 Å (–CH$_3$), and with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$.

References

Aarthi, R., Thiruvalluvar, A. & Ramachandra Raja, C. (2017). *IUCrData*, **2**, x171213.
Bruker (2016). *APEX3*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolbecq, A., Dumas, E., Mayer, C. R. & Mialane, P. (2010). *Chem. Rev.* **110**, 6009–6048.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.
Souissi, S., Smirani Sta, W., Al-Deyab, S. S. & Rzaigui, M. (2010). *Acta Cryst.* E**66**, o1627.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

(4-Methylphenyl)methanaminium bromide hemihydrate

R Aarthi, A Thiruvalluvar and C Ramachandra Raja

(4-Methylphenyl)methanaminium bromide hemihydrate

Crystal data

$C_8H_{12}N^+ \cdot Br^- \cdot 0.5(H_2O)$	$F(000) = 856$
$M_r = 211.10$	$D_x = 1.521$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 30.7456$ (18) Å	Cell parameters from 7215 reflections
$b = 5.0266$ (3) Å	$\theta = 3.4$–$29.2°$
$c = 12.0636$ (7) Å	$\mu = 4.40$ mm^{-1}
$\beta = 98.430$ (2)°	$T = 293$ K
$V = 1844.24$ (19) Å^3	Block, colourless
$Z = 8$	$0.10 \times 0.10 \times 0.05$ mm

Data collection

Bruker KappaCCD diffractometer	11261 measured reflections
Radiation source: fine-focus sealed tube	2479 independent reflections
Graphite monochromator	2129 reflections with $I > 2\sigma(I)$
ω and φ scan	$R_{int} = 0.025$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{max} = 29.2°$, $\theta_{min} = 3.5°$
$T_{min} = 0.534$, $T_{max} = 0.746$	$h = -40 \rightarrow 42$
	$k = -6 \rightarrow 6$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 2.3541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
2479 reflections	$(\Delta/\sigma)_{max} < 0.001$
113 parameters	$\Delta\rho_{max} = 0.35$ e Å^{-3}
7 restraints	$\Delta\rho_{min} = -0.51$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.27703 (8)	1.1301 (4)	0.6636 (2)	0.0494 (6)
H1A	0.286021	1.299079	0.637653	0.074*
H1B	0.275755	1.140043	0.742564	0.074*
H1C	0.248504	1.085224	0.624468	0.074*
C2	0.30965 (6)	0.9198 (4)	0.64201 (18)	0.0340 (4)
C3	0.31078 (7)	0.8211 (4)	0.53533 (18)	0.0406 (4)
H3	0.291045	0.886455	0.475733	0.049*
C4	0.34066 (7)	0.6273 (4)	0.51557 (17)	0.0399 (4)
H4	0.340822	0.565059	0.443038	0.048*
C5	0.37039 (6)	0.5248 (4)	0.60273 (17)	0.0321 (4)
C6	0.36998 (7)	0.6264 (4)	0.70908 (17)	0.0385 (4)
H6	0.390104	0.563229	0.768332	0.046*
C7	0.34002 (7)	0.8212 (4)	0.72890 (18)	0.0402 (4)
H7	0.340289	0.886252	0.801160	0.048*
C8	0.40117 (7)	0.3025 (4)	0.5831 (2)	0.0427 (5)
H8A	0.400833	0.169245	0.641177	0.051*
H8B	0.390675	0.219026	0.511705	0.051*
N1	0.44665 (6)	0.3933 (4)	0.58300 (18)	0.0420 (4)
Br1	0.44849 (2)	0.86079 (4)	0.38999 (2)	0.04217 (8)
O1	0.500000	0.2903 (5)	0.250000	0.0548 (6)
H1	0.4840 (11)	0.196 (6)	0.286 (3)	0.096 (13)*
H1D	0.4466 (9)	0.520 (4)	0.5282 (17)	0.065 (8)*
H1E	0.4585 (9)	0.465 (5)	0.6483 (14)	0.063 (8)*
H1F	0.4636 (9)	0.255 (4)	0.566 (2)	0.072 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0401 (11)	0.0394 (11)	0.0728 (16)	0.0092 (9)	0.0221 (11)	0.0048 (11)
C2	0.0284 (9)	0.0293 (8)	0.0465 (11)	0.0002 (7)	0.0126 (8)	0.0030 (8)
C3	0.0335 (10)	0.0479 (11)	0.0391 (10)	0.0058 (9)	0.0005 (8)	0.0056 (9)
C4	0.0382 (10)	0.0492 (11)	0.0330 (9)	0.0004 (9)	0.0073 (8)	−0.0061 (9)
C5	0.0274 (9)	0.0287 (8)	0.0416 (10)	−0.0015 (7)	0.0096 (7)	−0.0021 (7)
C6	0.0379 (10)	0.0410 (10)	0.0359 (9)	0.0089 (9)	0.0027 (8)	0.0029 (8)
C7	0.0459 (11)	0.0410 (10)	0.0348 (10)	0.0063 (9)	0.0096 (8)	−0.0016 (8)
C8	0.0373 (11)	0.0319 (9)	0.0615 (14)	0.0011 (8)	0.0165 (10)	−0.0053 (9)
N1	0.0315 (8)	0.0403 (9)	0.0550 (11)	0.0086 (8)	0.0094 (8)	0.0002 (9)
Br1	0.03836 (12)	0.03826 (12)	0.05064 (14)	0.00097 (9)	0.00907 (8)	−0.00115 (9)
O1	0.0631 (16)	0.0452 (13)	0.0609 (16)	0.000	0.0250 (13)	0.000

Geometric parameters (Å, º)

C1—C2	1.506 (3)	C6—C7	1.389 (3)
C1—H1A	0.9600	C6—H6	0.9300
C1—H1B	0.9600	C7—H7	0.9300

C1—H1C	0.9600	C8—N1	1.471 (3)
C2—C3	1.384 (3)	C8—H8A	0.9700
C2—C7	1.389 (3)	C8—H8B	0.9700
C3—C4	1.384 (3)	N1—H1D	0.919 (15)
C3—H3	0.9300	N1—H1E	0.895 (15)
C4—C5	1.387 (3)	N1—H1F	0.909 (15)
C4—H4	0.9300	O1—H1	0.848 (17)
C5—C6	1.383 (3)	O1—H1^i	0.848 (17)
C5—C8	1.505 (3)		

C2—C1—H1A	109.5	C5—C6—H6	119.4
C2—C1—H1B	109.5	C7—C6—H6	119.4
H1A—C1—H1B	109.5	C6—C7—C2	120.74 (19)
C2—C1—H1C	109.5	C6—C7—H7	119.6
H1A—C1—H1C	109.5	C2—C7—H7	119.6
H1B—C1—H1C	109.5	N1—C8—C5	112.91 (17)
C3—C2—C7	117.90 (18)	N1—C8—H8A	109.0
C3—C2—C1	121.4 (2)	C5—C8—H8A	109.0
C7—C2—C1	120.7 (2)	N1—C8—H8B	109.0
C4—C3—C2	121.34 (19)	C5—C8—H8B	109.0
C4—C3—H3	119.3	H8A—C8—H8B	107.8
C2—C3—H3	119.3	C8—N1—H1D	108.4 (18)
C3—C4—C5	120.75 (18)	C8—N1—H1E	113.0 (18)
C3—C4—H4	119.6	H1D—N1—H1E	108.0 (19)
C5—C4—H4	119.6	C8—N1—H1F	109.8 (19)
C6—C5—C4	118.12 (18)	H1D—N1—H1F	107.9 (19)
C6—C5—C8	120.76 (19)	H1E—N1—H1F	110 (2)
C4—C5—C8	121.08 (19)	H1—O1—H1^i	112 (5)
C5—C6—C7	121.11 (19)		

C7—C2—C3—C4	1.0 (3)	C8—C5—C6—C7	−176.38 (19)
C1—C2—C3—C4	−179.8 (2)	C5—C6—C7—C2	−0.2 (3)
C2—C3—C4—C5	0.3 (3)	C3—C2—C7—C6	−1.1 (3)
C3—C4—C5—C6	−1.6 (3)	C1—C2—C7—C6	179.71 (19)
C3—C4—C5—C8	176.30 (19)	C6—C5—C8—N1	−77.2 (3)
C4—C5—C6—C7	1.5 (3)	C4—C5—C8—N1	105.0 (2)

Symmetry code: (i) −x+1, y, −z+1/2.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the (C2–C7) benzene ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯Br1^{ii}	0.85 (2)	2.45 (2)	3.2870 (17)	169 (3)
N1—H1D⋯Br1	0.92 (2)	2.40 (2)	3.314 (2)	178 (2)
N1—H1E⋯O1^{iii}	0.90 (2)	2.05 (2)	2.883 (3)	155 (2)
N1—H1F⋯Br1^{ii}	0.91 (2)	2.89 (2)	3.554 (2)	131 (2)
N1—H1F⋯Br1^{iii}	0.91 (2)	2.74 (3)	3.4383 (17)	134 (2)

C8—H8*B*···Br1[ii]	0.97	3.05	3.670 (2)	123
C1—H1*A*···*Cg*1[iv]	0.96	2.73	3.634 (2)	157
C8—H8*A*···*Cg*1[ii]	0.97	2.90	3.530 (2)	123

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