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1,1′-Dimethyl-1,1′-(butane-1,4-diyl)-dipyrrolidinium dibromide methanol disolvate

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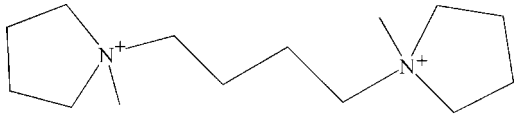
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.067; data-to-parameter ratio = 20.2.

In the title compound, $C_{14}H_{30}N_2^{2+}\cdot 2Br^-\cdot 2CH_3OH$, two terminal C atoms of the butane chain are connected to two N atoms of the 1-methylpyrollidines, forming a linear diquaternary ammonium cation. The cation lies across a centre of inversion located between the two central C atoms of the butane chain. The asymmetric unit therefore comprises one half-cation, a bromide anion and a methanol solvent molecule. In the crystal structure, the bromide anions are linked to the methanol solvent molecules by O—H···Br hydrogen bonds.

Related literature

For information on the use of organic amines in zeolite synthesis, see: Gramm *et al.* (2006); Hong *et al.* (2007). For a previous synthesis of the title compound, see: Hong *et al.* (2004).



$\cdot 2CH_3OH\ \cdot 2Br^-$

Experimental

Crystal data

$C_{14}H_{30}N_2^{2+}\cdot 2Br^-\cdot 2CH_4O$
M_r = 450.30
Monoclinic, $P2_1/n$
a = 6.4919 (7) Å
b = 12.4861 (13) Å
c = 12.9683 (13) Å
β = 90.748 (2)°
V = 1051.10 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.87 mm^{-1}
T = 193 (2) K
0.30 × 0.25 × 0.24 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.390, T_{max} = 0.457
(expected range = 0.337–0.396)
5618 measured reflections
2013 independent reflections
1681 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.067
S = 1.09
2013 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Br1	0.82	2.43	3.2453 (18)	172

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2458).

References

Bruker (2000). *SMART* (Version 5.625) and *SAINT* (Version 6.01) and *SADABS* **(Version?)**. Bruker AXS Inc., Madison, Wisconsin, USA.
Gramm, F., Baerlocher, C., McCusker, L. B., Warrender, S. J., Wright, P. A., Han, B., Hong, S. B., Liu, Z., Ohsuna, T. & Terasaki, O. (2006). *Nature (London)*, **444**, 79–81.
Hong, S. B., Lear, E. G., Wright, P. A., Zhou, W. Z., Cox, P. A., Shin, C. H., Park, J. H. & Nam, I. S. (2004). *J. Am. Chem. Soc.* **126**, 5817–5826.
Hong, S. B., Min, H. K., Shin, C. H., Cox, P. A., Warrender, S. J. & Wright, P. A. (2007). *J. Am. Chem. Soc.* **129**, 10870–10885.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2008). E**64**, o417 [doi:10.1107/S1600536808000172]

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S1. Comment

The use of zeolites as catalysts or catalyst supports is now widely applied in petrochemical and fine chemical processes. The synthesis of zeolites involves the addition of organic amines and it is proposed that in most cases, the amine acts as a structure-directing agent, helping to shape the framework of the structure. TNU-9 is a complex zeolite (Gramm *et al.*, 2006) and the title compound, (I), is used as structure-directing agent in the synthesis of the TNU-9 zeolite (Hong *et al.*, 2007). In this paper, we report a modified synthesis and the crystal structure of (I), Fig 1.

The structure of (I) consists of a linear diquaternary ammonium cation, two bromide anions and two methanol solvate molecules. The cation lies about an inversion centre at the centroid of the C6—C6A bond in the butane chain. The terminal carbon atoms of the butane are connected to the N atoms of the 1-methylpyrolidines, forming a linear diquaternary ammonium cation. In the crystal structure Br^- anions are linked to methanol molecules by O1—H1···Br1 hydrogen bonds that stabilize the structure (Fig 2, Table 1).

S2. Experimental

(I) was prepared by refluxing 1,4-dibromobutane (1 mmol, 99%, Arcos) with an excess of 1-methylpyrrolidine (3 mmol, 97%, Arcos) 24 h in acetone (150 ml, 99%, Arcos), in a modification of the previously reported procedure (Hong *et al.*, 2004). The excess amine was removed by extraction with acetone, and recrystallizations were performed in a methanol-diethylether mixtures (2:1).

S3. Refinement

H atoms were positioned geometrically with O—H = 0.82 and C—H = 0.96–0.97 Å, and allowed to ride on their parent atoms with U_{iso}(H) = 1.2 U_{eq}(C) for CH_2 groups, and 1.5 U_{eq}(C,*O*) for the –OH and –CH_3 groups.

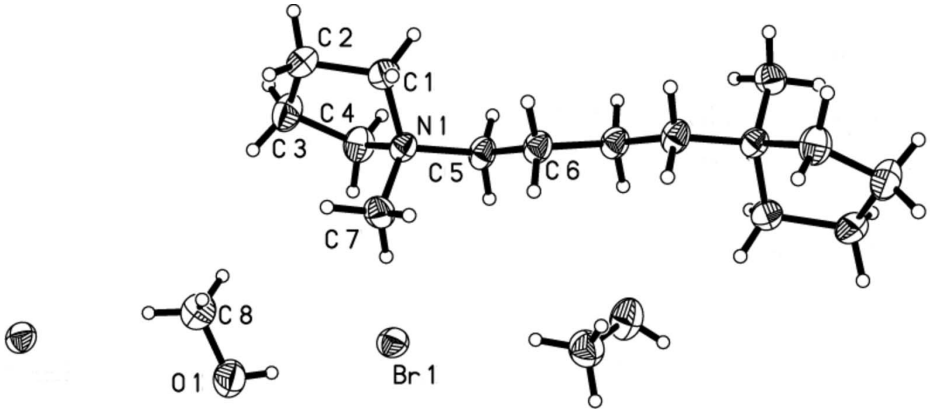

Figure 1

View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation-x + 1,-y,-z + 2.

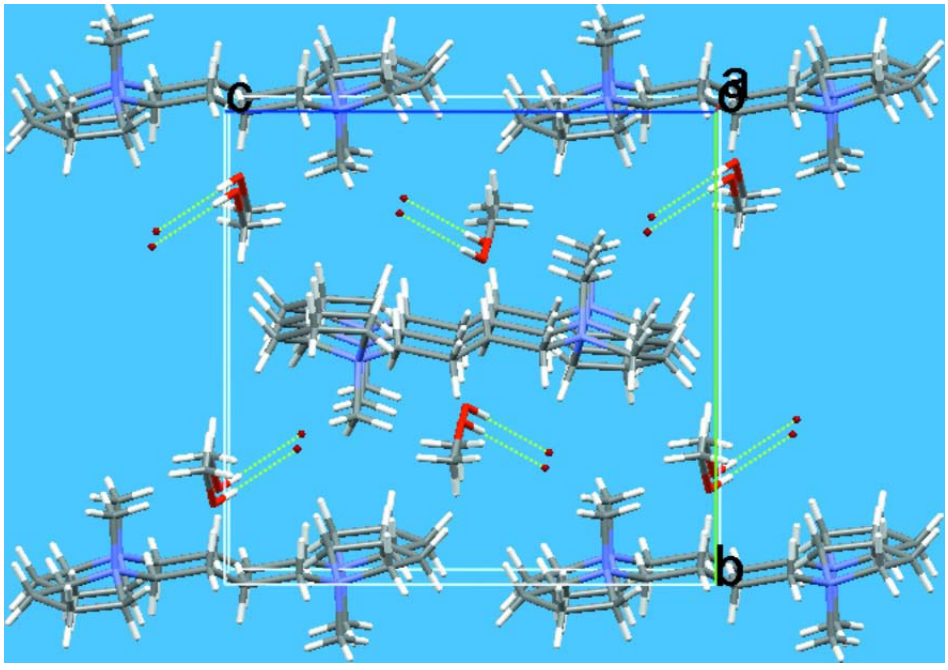

Figure 2

The molecular packing of (I) with hydrogen bonds drawn as dashed lines.

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Crystal data

$C_{14}H_{30}N_2^{2+}\cdot 2Br^-\cdot 2CH_4O$
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Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.4919 (7) Å
b = 12.4861 (13) Å
c = 12.9683 (13) Å
β = 90.748 (2)°
V = 1051.10 (19) Å^3
Z = 2
F(000) = 468
D_x = 1.423 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5618 reflections
θ = 2.3–26.0°
μ = 3.87 mm^{-1}

T = 193 K
Block, colorless
0.30 × 0.25 × 0.24 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.390, T_{max} = 0.457
5618 measured reflections
2013 independent reflections
1681 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 26.0°, θ_{min} = 2.3°
$h = -5 \rightarrow 8$
$k = -14 \rightarrow 15$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.067
S = 1.09
2013 reflections
102 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.1193P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.22798 (4)	0.222545 (19)	0.645609 (19)	0.03899 (11)
N1	0.6827 (3)	0.01906 (14)	0.77454 (14)	0.0279 (4)
C1	0.8754 (4)	−0.04680 (19)	0.79320 (18)	0.0380 (6)
H1A	0.8411	−0.1171	0.8198	0.046*
H1B	0.9671	−0.0113	0.8420	0.046*
C2	0.9755 (4)	−0.0559 (2)	0.68752 (18)	0.0443 (7)
H2A	1.0286	−0.1276	0.6772	0.053*
H2B	1.0884	−0.0054	0.6820	0.053*
C3	0.8074 (4)	−0.0306 (2)	0.60735 (19)	0.0467 (7)
H3A	0.8386	0.0351	0.5708	0.056*
H3B	0.7939	−0.0884	0.5577	0.056*
C4	0.6110 (4)	−0.0184 (2)	0.66926 (17)	0.0385 (6)
H4A	0.5197	0.0339	0.6375	0.046*
H4B	0.5390	−0.0862	0.6741	0.046*

C5	0.5187 (3)	−0.00229 (18)	0.85296 (17)	0.0316 (5)
H5A	0.4768	−0.0767	0.8475	0.038*
H5B	0.3994	0.0415	0.8364	0.038*
C6	0.5842 (3)	0.01998 (18)	0.96372 (16)	0.0319 (5)
H6A	0.6052	0.0962	0.9734	0.038*
H6B	0.7129	−0.0164	0.9792	0.038*
C7	0.7340 (4)	0.13607 (17)	0.77065 (18)	0.0344 (5)
H7A	0.7800	0.1595	0.8376	0.052*
H7B	0.6137	0.1759	0.7503	0.052*
H7C	0.8412	0.1477	0.7216	0.052*
O1	0.5324 (3)	0.32947 (15)	0.47786 (14)	0.0510 (5)
H1	0.4456	0.3057	0.5171	0.076*
C8	0.6858 (4)	0.2517 (2)	0.4620 (2)	0.0478 (7)
H8A	0.7952	0.2615	0.5116	0.072*
H8B	0.7392	0.2590	0.3937	0.072*
H8C	0.6275	0.1816	0.4700	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03054 (16)	0.03698 (16)	0.04954 (18)	0.00222 (11)	0.00417 (11)	0.00310 (11)
N1	0.0241 (10)	0.0302 (9)	0.0296 (10)	0.0005 (8)	0.0036 (8)	−0.0010 (8)
C1	0.0336 (13)	0.0414 (14)	0.0390 (14)	0.0110 (11)	0.0052 (11)	0.0050 (11)
C2	0.0438 (16)	0.0413 (14)	0.0482 (16)	0.0130 (12)	0.0163 (13)	0.0038 (12)
C3	0.0487 (16)	0.0560 (17)	0.0359 (14)	0.0039 (14)	0.0113 (13)	−0.0063 (12)
C4	0.0396 (14)	0.0453 (14)	0.0307 (12)	−0.0027 (12)	−0.0011 (11)	−0.0059 (11)
C5	0.0243 (12)	0.0349 (12)	0.0359 (13)	−0.0060 (10)	0.0079 (10)	−0.0032 (10)
C6	0.0265 (12)	0.0337 (12)	0.0356 (13)	−0.0031 (10)	0.0072 (10)	−0.0019 (10)
C7	0.0318 (13)	0.0308 (12)	0.0406 (14)	−0.0050 (10)	0.0041 (11)	0.0040 (10)
O1	0.0450 (12)	0.0590 (12)	0.0492 (12)	0.0083 (10)	0.0092 (9)	0.0080 (9)
C8	0.0447 (17)	0.0497 (15)	0.0492 (17)	0.0009 (13)	0.0048 (14)	−0.0040 (12)

Geometric parameters (Å, º)

N1—C7	1.500 (3)	C5—C6	1.518 (3)
N1—C5	1.506 (3)	C5—H5A	0.9700
N1—C4	1.511 (3)	C5—H5B	0.9700
N1—C1	1.514 (3)	C6—C6^{i}	1.535 (4)
C1—C2	1.528 (3)	C6—H6A	0.9700
C1—H1A	0.9700	C6—H6B	0.9700
C1—H1B	0.9700	C7—H7A	0.9600
C2—C3	1.530 (4)	C7—H7B	0.9600
C2—H2A	0.9700	C7—H7C	0.9600
C2—H2B	0.9700	O1—C8	1.408 (3)
C3—C4	1.523 (3)	O1—H1	0.8200
C3—H3A	0.9700	C8—H8A	0.9600
C3—H3B	0.9700	C8—H8B	0.9600
C4—H4A	0.9700	C8—H8C	0.9600

C4—H4B	0.9700		
C7—N1—C5	110.76 (17)	C3—C4—H4B	110.8
C7—N1—C4	109.70 (18)	H4A—C4—H4B	108.8
C5—N1—C4	110.08 (17)	N1—C5—C6	114.51 (17)
C7—N1—C1	110.55 (18)	N1—C5—H5A	108.6
C5—N1—C1	112.72 (17)	C6—C5—H5A	108.6
C4—N1—C1	102.75 (17)	N1—C5—H5B	108.6
N1—C1—C2	104.89 (18)	C6—C5—H5B	108.6
N1—C1—H1A	110.8	H5A—C5—H5B	107.6
C2—C1—H1A	110.8	C5—C6—C6^{i}	109.1 (2)
N1—C1—H1B	110.8	C5—C6—H6A	109.9
C2—C1—H1B	110.8	C6^{i}—C6—H6A	109.9
H1A—C1—H1B	108.8	C5—C6—H6B	109.9
C1—C2—C3	106.6 (2)	C6^{i}—C6—H6B	109.9
C1—C2—H2A	110.4	H6A—C6—H6B	108.3
C3—C2—H2A	110.4	N1—C7—H7A	109.5
C1—C2—H2B	110.4	N1—C7—H7B	109.5
C3—C2—H2B	110.4	H7A—C7—H7B	109.5
H2A—C2—H2B	108.6	N1—C7—H7C	109.5
C4—C3—C2	104.9 (2)	H7A—C7—H7C	109.5
C4—C3—H3A	110.8	H7B—C7—H7C	109.5
C2—C3—H3A	110.8	C8—O1—H1	109.5
C4—C3—H3B	110.8	O1—C8—H8A	109.5
C2—C3—H3B	110.8	O1—C8—H8B	109.5
H3A—C3—H3B	108.8	H8A—C8—H8B	109.5
N1—C4—C3	104.9 (2)	O1—C8—H8C	109.5
N1—C4—H4A	110.8	H8A—C8—H8C	109.5
C3—C4—H4A	110.8	H8B—C8—H8C	109.5
N1—C4—H4B	110.8		

Symmetry code: (i) $-x+1, -y, -z+2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Br1	0.82	2.43	3.2453 (18)	172