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4-Benzylpiperazin-1-ium chloride chloroform solvate

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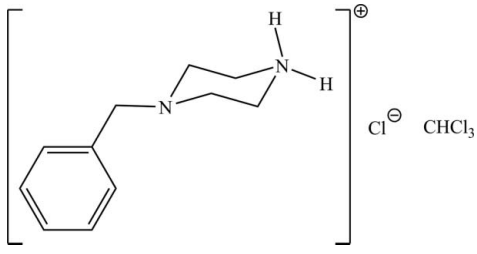
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.128; data-to-parameter ratio = 17.0.

The ions of the title chloroform-solvated salt, $C_{11}H_{17}N_2^+\cdot Cl^-\cdot CHCl_3$, are linked by a strong N—H···Cl hydrogen bond; the solvent molecule also interacts with the chloride ion through a C—H···Cl hydrogen bond. Additionally, neighboring cations form weak hydrogen bonds to the anion, resulting in a supramolecular ribbon that runs along the *a* axis.

Related literature

For related literature, see Albinati *et al.* (1980); Antolini *et al.* (1981, 1982); Osa *et al.* (2002); Tanaka *et al.* (2005).



Experimental

Crystal data

$C_{11}H_{17}N_2^+\cdot Cl^-\cdot CHCl_3$
M_r = 332.08
Triclinic, $P\overline{1}$
a = 5.6053 (4) Å
b = 9.4889 (9) Å
c = 15.303 (2) Å
α = 100.980 (8)°
β = 90.957 (7)°
γ = 93.219 (7)°
V = 797.51 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.73 mm^{-1}
T = 173 (2) K
0.40 × 0.32 × 0.30 mm

Data collection

Siemens P4 diffractometer
Absorption correction: none
4013 measured reflections
2967 independent reflections
2811 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
3 standard reflections
every 197 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.128
S = 1.07
2967 reflections
175 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N···Cl1	0.85 (2)	2.30 (2)	3.140 (2)	169 (2)
C12—H12···Cl1	0.89 (3)	2.60 (3)	3.401 (2)	151 (2)
N2—H2N···Cl1^{i}	0.88 (2)	2.26 (2)	3.096 (2)	159 (2)
C10—H10A···Cl1^{ii}	0.97	2.74	3.684 (2)	165

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

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2473).

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supporting information

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4-Benzylpiperazin-1-ium chloride chloroform solvate

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S1. Comment

Derivatives of piperazine are useful compounds because of their biological activity (Osa *et al.*, 2002). Trimetazidine is a clinically antianginal agent (Tanaka *et al.*, 2005). A compound of the type $(NBzpipzH_2)_2CuCl_6$ ($NBzpipzH_2$ = *N*-benzylpiperazinium dication) was reported (Antolini *et al.*, 1982) and the preparation of mercury(III) compounds $(NbzpipzH)Hg_2X_5$ (NbzpipzH = *N*-benzylpiperazinium monocation; *X* = Cl, Br) is known (Albinati, *et al.*, 1980, Antolini *et al.*, 1981).

The title compound (Fig.1) is formed by $C_{11}H_{17}N_2^+$ cation and Cl^- anion connected through a strong N—H···Cl^- hydrogen bond [H1N···Cl1 = 2.30 (2) Å, N2—H1N···Cl1 = 169 (2)°] and crystallizes with a $CHCl_3$ molecule bonded to the Cl^- through a hydrogen bond [H12···Cl1 = 2.60 (3) Å, C12—H12···Cl1 = 151 (2)°]. Intermolecular hydrogen bonds link the Cl^- anion to two aditional cations (Table 1) resulting in a double chain-like supramolecular arrangement along the *a* axis. In crystal there are no interactions between the chains (Fig.2).

S2. Experimental

The compound was obtained as a by-product of the reaction between $[2\text{-}\{HN(CH_2CH_2)_2NCH_2\}C_6H_4]Li$ and $BiCl_3$. Crystals were grown by slow difusion from chloroform / n-hexane (1:5).

^{1}H NMR ($CDCl_3$, 200 MHz, 291 K): δ 2.74 (4*H*, *m*, N—CH_2—CH_2—N), 3.20 (4*H*, *m*, N—CH_2—CH_2—N), 3.55 (2*H*, *s*, C_6H_5—CH_2—N), 7.29 (5*H*, *m*, C_6H_5), 8.90 (2*H*, *s*, br, NH_2). ^{13}C NMR ($CDCl_3$, 50 MHz, 291 K): δ 43.59 (*s*, N—CH_2—CH_2—N), 49.47 (*s*, N—CH_2—CH_2—N), 62.39 (*s*, C_6H_5—CH_2—N), 127.53 (*s*, C-p), 128.45 (*s*, C-m), 128.95 (*s*, C-o), 136.89 (*s*, C-i).

S3. Refinement

All hydrogen atoms were placed in calculated positions using a riding model, with C—H = 0.93–0.97 Å and with U_{iso}= 1.2U_{eq} (C) for aryl H and U_{iso}= 1.5U_{eq} (C) for the rest. The hydrogen H1N, H2N and H12 atoms bonded to N2 and C12, respectively, were found in a difference map and refined with a restrained N—H distance of 0.85 (2) and 0.88 (2) Å, and C—H distance of 0.89 (3) Å, respectively.

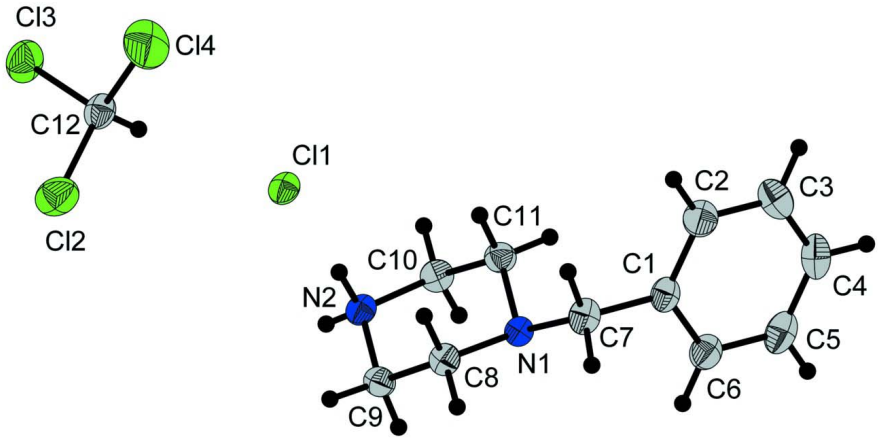

Figure 1

View of the title compound showing the atom-numbering (50% probability thermal ellipsoids).

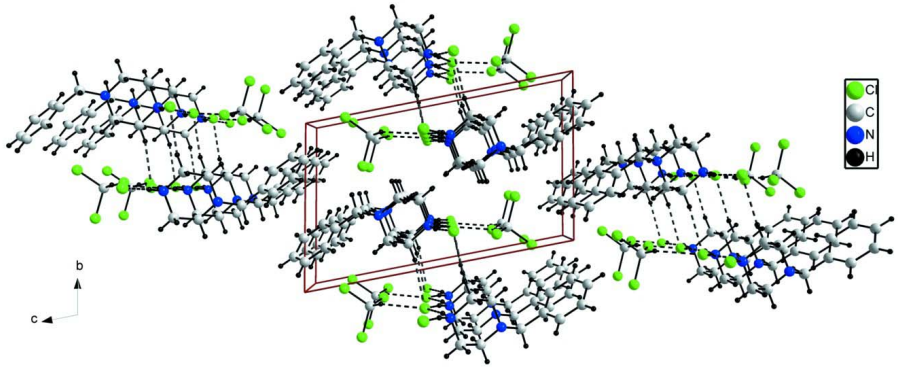

Figure 2

Crystal packing of the title compound showing the supramolecular arrays (hydrogen bonds as dashes lines).

4-Benzylpiperazin-1-ium chloride chloroform solvate

Crystal data

$C_{11}H_{17}N_2^+ \cdot Cl^- \cdot CHCl_3$
$M_r = 332.08$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.6053\ (4)$ Å
$b = 9.4889\ (9)$ Å
$c = 15.303\ (2)$ Å
$\alpha = 100.980\ (8)°$
$\beta = 90.957\ (7)°$
$\gamma = 93.219\ (7)°$
$V = 797.51\ (15)$ Å^3
$Z = 2$
$F(000) = 344$
$D_x = 1.383$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 8.5–25.1°$
$\mu = 0.73$ mm^{-1}
$T = 173$ K
Block, colorless
0.40 × 0.32 × 0.30 mm

Data collection

Siemens P4 diffractometer
Radiation source: sealed tube
Graphite monochromator
$2\theta–/\omega$ scans
4013 measured reflections
2967 independent reflections
2811 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.7°$
$h = -6\rightarrow2$
$k = -11\rightarrow11$
$l = -18\rightarrow18$
3 standard reflections every 197 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.128$
$S = 1.07$
2967 reflections
175 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 0.5046P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl4	1.23828 (12)	0.13191 (10)	0.29039 (5)	0.0610 (2)
C12	0.9555 (4)	0.1520 (2)	0.24518 (15)	0.0300 (5)
Cl1	0.70662 (8)	0.21020 (5)	0.44910 (3)	0.02735 (17)
Cl2	0.94353 (13)	0.32245 (6)	0.21628 (5)	0.0472 (2)
Cl3	0.87877 (13)	0.01645 (7)	0.15238 (4)	0.0450 (2)
N1	0.3777 (3)	0.37270 (18)	0.71793 (11)	0.0228 (4)
N2	0.2108 (3)	0.25651 (19)	0.53939 (12)	0.0251 (4)
C2	0.6514 (4)	0.2552 (3)	0.89764 (16)	0.0353 (5)
H2	0.7872	0.2308	0.8654	0.042*
C6	0.2964 (4)	0.3838 (3)	0.91871 (15)	0.0324 (5)
H6	0.1924	0.4466	0.9010	0.039*
C11	0.3743 (4)	0.2181 (2)	0.68279 (14)	0.0275 (4)
H11A	0.3486	0.1659	0.7308	0.033*
H11B	0.5274	0.1940	0.6572	0.033*
C1	0.5004 (4)	0.3496 (2)	0.87052 (13)	0.0264 (4)
C8	0.4281 (4)	0.4505 (2)	0.64568 (14)	0.0260 (4)
H8A	0.5804	0.4242	0.6202	0.031*
H8B	0.4386	0.5531	0.6690	0.031*
C9	0.2325 (4)	0.4145 (2)	0.57441 (14)	0.0273 (4)
H9A	0.0819	0.4460	0.5991	0.033*
H9B	0.2689	0.4647	0.5262	0.033*
C5	0.2475 (4)	0.3245 (3)	0.99313 (16)	0.0380 (5)
H5	0.1106	0.3477	1.0249	0.046*
C10	0.1780 (4)	0.1739 (2)	0.61243 (14)	0.0280 (4)

H10A	0.1808	0.0718	0.5884	0.034*
H10B	0.0239	0.1917	0.6389	0.034*
C4	0.4008 (5)	0.2314 (3)	1.02029 (15)	0.0389 (6)
H4	0.3681	0.1925	1.0705	0.047*
C7	0.5559 (4)	0.4164 (2)	0.79057 (14)	0.0286 (5)
H7A	0.5634	0.5203	0.8085	0.034*
H7B	0.7117	0.3888	0.7691	0.034*
C3	0.6033 (5)	0.1962 (3)	0.97243 (17)	0.0415 (6)
H3	0.7071	0.1332	0.9902	0.050*
H1N	0.339 (4)	0.232 (3)	0.5127 (17)	0.035 (7)*
H2N	0.089 (4)	0.235 (3)	0.5012 (16)	0.039 (7)*
H12	0.848 (5)	0.145 (3)	0.2865 (19)	0.039 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl4	0.0309 (4)	0.0937 (6)	0.0588 (5)	0.0100 (3)	−0.0096 (3)	0.0144 (4)
C12	0.0240 (10)	0.0381 (12)	0.0271 (10)	0.0006 (9)	0.0046 (9)	0.0044 (9)
Cl1	0.0176 (3)	0.0367 (3)	0.0265 (3)	0.0034 (2)	0.00211 (19)	0.0023 (2)
Cl2	0.0565 (4)	0.0326 (3)	0.0527 (4)	0.0009 (3)	0.0136 (3)	0.0079 (3)
Cl3	0.0589 (4)	0.0362 (3)	0.0360 (3)	−0.0047 (3)	−0.0030 (3)	−0.0007 (2)
N1	0.0214 (8)	0.0232 (8)	0.0230 (8)	−0.0007 (6)	0.0010 (7)	0.0032 (6)
N2	0.0167 (8)	0.0323 (9)	0.0248 (9)	0.0026 (7)	0.0004 (7)	0.0014 (7)
C2	0.0256 (11)	0.0460 (13)	0.0335 (12)	0.0042 (9)	−0.0001 (9)	0.0053 (10)
C6	0.0274 (11)	0.0396 (12)	0.0286 (11)	0.0031 (9)	−0.0004 (9)	0.0020 (9)
C11	0.0290 (11)	0.0248 (10)	0.0283 (10)	0.0021 (8)	−0.0002 (8)	0.0043 (8)
C1	0.0231 (10)	0.0306 (10)	0.0226 (10)	−0.0044 (8)	−0.0037 (8)	0.0001 (8)
C8	0.0254 (10)	0.0253 (10)	0.0272 (10)	−0.0021 (8)	0.0027 (8)	0.0056 (8)
C9	0.0264 (10)	0.0274 (10)	0.0291 (10)	0.0035 (8)	0.0008 (8)	0.0074 (8)
C5	0.0335 (12)	0.0491 (14)	0.0282 (11)	−0.0033 (10)	0.0062 (9)	0.0003 (10)
C10	0.0268 (10)	0.0250 (10)	0.0312 (11)	−0.0029 (8)	0.0000 (8)	0.0040 (8)
C4	0.0443 (14)	0.0468 (13)	0.0246 (10)	−0.0096 (11)	−0.0027 (10)	0.0082 (10)
C7	0.0230 (10)	0.0333 (11)	0.0273 (10)	−0.0053 (8)	−0.0017 (8)	0.0023 (9)
C3	0.0418 (14)	0.0471 (14)	0.0380 (13)	0.0035 (11)	−0.0078 (11)	0.0146 (11)

Geometric parameters (Å, º)

Cl4—C12	1.753 (2)	C11—H11A	0.9700
C12—Cl3	1.755 (2)	C11—H11B	0.9700
C12—Cl2	1.761 (2)	C1—C7	1.510 (3)
C12—H12	0.89 (3)	C8—C9	1.511 (3)
N1—C11	1.462 (3)	C8—H8A	0.9700
N1—C8	1.464 (2)	C8—H8B	0.9700
N1—C7	1.465 (3)	C9—H9A	0.9700
N2—C9	1.490 (3)	C9—H9B	0.9700
N2—C10	1.491 (3)	C5—C4	1.381 (4)
N2—H1N	0.852 (17)	C5—H5	0.9300
N2—H2N	0.881 (17)	C10—H10A	0.9700

C2—C1	1.381 (3)	C10—H10B	0.9700
C2—C3	1.391 (3)	C4—C3	1.383 (4)
C2—H2	0.9300	C4—H4	0.9300
C6—C5	1.387 (3)	C7—H7A	0.9700
C6—C1	1.391 (3)	C7—H7B	0.9700
C6—H6	0.9300	C3—H3	0.9300
C11—C10	1.511 (3)		

Cl4—C12—Cl3	111.93 (13)	C9—C8—H8A	109.6
Cl4—C12—Cl2	110.52 (13)	N1—C8—H8B	109.6
Cl3—C12—Cl2	110.17 (12)	C9—C8—H8B	109.6
Cl4—C12—H12	108.1 (19)	H8A—C8—H8B	108.2
Cl3—C12—H12	107.5 (19)	N2—C9—C8	110.19 (16)
Cl2—C12—H12	108.5 (18)	N2—C9—H9A	109.6
C11—N1—C8	109.08 (16)	C8—C9—H9A	109.6
C11—N1—C7	111.36 (16)	N2—C9—H9B	109.6
C8—N1—C7	110.31 (16)	C8—C9—H9B	109.6
C9—N2—C10	111.57 (16)	H9A—C9—H9B	108.1
C9—N2—H1N	108.5 (19)	C4—C5—C6	120.4 (2)
C10—N2—H1N	108.6 (18)	C4—C5—H5	119.8
C9—N2—H2N	109.8 (18)	C6—C5—H5	119.8
C10—N2—H2N	109.3 (18)	N2—C10—C11	110.24 (17)
H1N—N2—H2N	109 (3)	N2—C10—H10A	109.6
C1—C2—C3	120.9 (2)	C11—C10—H10A	109.6
C1—C2—H2	119.5	N2—C10—H10B	109.6
C3—C2—H2	119.5	C11—C10—H10B	109.6
C5—C6—C1	120.3 (2)	H10A—C10—H10B	108.1
C5—C6—H6	119.8	C5—C4—C3	119.6 (2)
C1—C6—H6	119.8	C5—C4—H4	120.2
N1—C11—C10	110.42 (17)	C3—C4—H4	120.2
N1—C11—H11A	109.6	N1—C7—C1	112.66 (17)
C10—C11—H11A	109.6	N1—C7—H7A	109.1
N1—C11—H11B	109.6	C1—C7—H7A	109.1
C10—C11—H11B	109.6	N1—C7—H7B	109.1
H11A—C11—H11B	108.1	C1—C7—H7B	109.1
C2—C1—C6	118.9 (2)	H7A—C7—H7B	107.8
C2—C1—C7	120.9 (2)	C4—C3—C2	119.8 (2)
C6—C1—C7	120.3 (2)	C4—C3—H3	120.1
N1—C8—C9	110.12 (16)	C2—C3—H3	120.1
N1—C8—H8A	109.6		

C8—N1—C11—C10	−61.9 (2)	C1—C6—C5—C4	0.1 (4)
C7—N1—C11—C10	176.10 (16)	C9—N2—C10—C11	−53.5 (2)
C3—C2—C1—C6	−0.8 (3)	N1—C11—C10—N2	57.5 (2)
C3—C2—C1—C7	178.5 (2)	C6—C5—C4—C3	−0.5 (4)
C5—C6—C1—C2	0.5 (3)	C11—N1—C7—C1	−63.9 (2)
C5—C6—C1—C7	−178.8 (2)	C8—N1—C7—C1	174.83 (17)
C11—N1—C8—C9	62.1 (2)	C2—C1—C7—N1	115.9 (2)

C7—N1—C8—C9	−175.25 (17)	C6—C1—C7—N1	−64.7 (3)
C10—N2—C9—C8	53.8 (2)	C5—C4—C3—C2	0.2 (4)
N1—C8—C9—N2	−58.0 (2)	C1—C2—C3—C4	0.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*···Cl1	0.85 (2)	2.30 (2)	3.140 (2)	169 (2)
C12—H12···Cl1	0.89 (3)	2.60 (3)	3.401 (2)	151 (2)
N2—H2*N*···Cl1^{i}	0.88 (2)	2.26 (2)	3.096 (2)	159 (2)
C10—H10*A*···Cl1^{ii}	0.97	2.74	3.684 (2)	165

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