

## 4-Benzylpiperazin-1-ium chloride chloroform solvate

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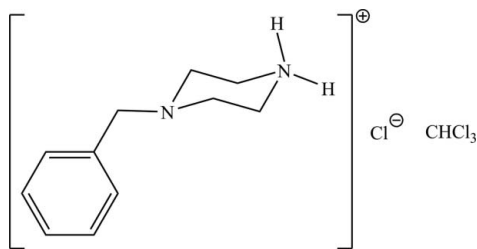
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.128; data-to-parameter ratio = 17.0.

The ions of the title chloroform-solvated salt,  $\text{C}_{11}\text{H}_{17}\text{N}_2^+\cdot\text{Cl}^-\cdot\text{CHCl}_3$ , are linked by a strong  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bond; the solvent molecule also interacts with the chloride ion through a  $\text{C}-\text{H}\cdots\text{Cl}$  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

$\text{C}_{11}\text{H}_{17}\text{N}_2^+\cdot\text{Cl}^-\cdot\text{CHCl}_3$   
 $M_r = 332.08$   
 Triclinic,  $P\bar{1}$   
 $a = 5.6053$  (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<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.73$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.40 \times 0.32 \times 0.30$  mm

#### Data collection

Siemens P4 diffractometer  
 Absorption correction: none  
 4013 measured reflections  
 2967 independent reflections  
 2811 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$   
 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  
 $\Delta\rho_{\text{max}} = 0.56$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.72$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}1\text{N}\cdots\text{Cl}1$	0.85 (2)	2.30 (2)	3.140 (2)	169 (2)
$\text{C}12-\text{H}12\cdots\text{Cl}1$	0.89 (3)	2.60 (3)	3.401 (2)	151 (2)
$\text{N}2-\text{H}2\text{N}\cdots\text{Cl}1^{\text{i}}$	0.88 (2)	2.26 (2)	3.096 (2)	159 (2)
$\text{C}10-\text{H}10\text{A}\cdots\text{Cl}1^{\text{ii}}$	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).

### References

- Albinati, A., Meille, S. V., Cariati, F., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1980). *Inorg. Chim. Acta*, **38**, 221–226.  
 Antolini, L., Menabue, L., Pellacani, G. C., Saladini, M. & Marcotrigiano, G. (1982). *Inorg. Chim. Acta*, **58**, 193–200.  
 Antolini, L., Menabue, L., Pellacani, G. C., Saladini, M., Marcotrigiano, G. & Porzio, W. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1753–1759.  
 Brandenburg, K. & Putz, H. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Osa, Y., Sato, Y., Hatano, A. & Takayanagi, T. (2002). *Anal. Sci.* **18**, 1069–1070.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Siemens (1994). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Tanaka, R., Haramura, M., Tanaka, A. & Hirayama, N. (2005). *X-ray Struct. Anal. Online*, **21**, x3–x4.  
 Westrip, S. P. (2008). *publCIF*. In preparation.

**supplementary materials**

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## 4-Benzylpiperazin-1-ium chloride chloroform solvate

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### 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<sub>2</sub>)<sub>2</sub>CuCl<sub>6</sub> (NBzpipzH<sub>2</sub> = *N*-benzylpiperazinium dication) was reported (Antolini *et al.*, 1982) and the preparation of mercury(III) compounds (NbzpipzH)Hg<sub>2</sub>X<sub>5</sub> (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<sub>11</sub>H<sub>17</sub>N<sub>2</sub><sup>+</sup> cation and Cl<sup>-</sup> anion connected through a strong N—H⋯Cl<sup>-</sup> hydrogen bond [H1N⋯Cl1 = 2.30 (2) Å, N2—H1N⋯Cl1 = 169 (2)°] and crystallizes with a CHCl<sub>3</sub> molecule bonded to the Cl<sup>-</sup> through a hydrogen bond [H12⋯Cl1 = 2.60 (3) Å, C12—H12⋯Cl1 = 151 (2)°]. Intermolecular hydrogen bonds link the Cl<sup>-</sup> anion to two additional 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).

### Experimental

The compound was obtained as a by-product of the reaction between [2-{HN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]Li and BiCl<sub>3</sub>. Crystals were grown by slow diffusion from chloroform / n-hexane (1:5).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, 291 K): δ 2.74 (4H, *m*, N—CH<sub>2</sub>—CH<sub>2</sub>—N), 3.20 (4H, *m*, N—CH<sub>2</sub>—CH<sub>2</sub>—N), 3.55 (2H, *s*, C<sub>6</sub>H<sub>5</sub>—CH<sub>2</sub>—N), 7.29 (5H, *m*, C<sub>6</sub>H<sub>5</sub>), 8.90 (2H, *s*, br, NH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, 291 K): δ 43.59 (*s*, N—CH<sub>2</sub>—CH<sub>2</sub>—N), 49.47 (*s*, N—CH<sub>2</sub>—CH<sub>2</sub>—N), 62.39 (*s*, C<sub>6</sub>H<sub>5</sub>—CH<sub>2</sub>—N), 127.53 (*s*, C-p), 128.45 (*s*, C-m), 128.95 (*s*, C-o), 136.89 (*s*, C-i).

### 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.

## Figures

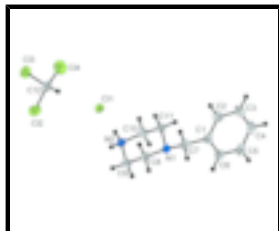


Fig. 1. : View of the title compound showing the atom-numbering (50% probability thermal ellipsoids).

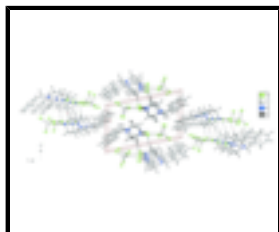


Fig. 2. : Crystal packing of the title compound showing the supramolecular arrays (hydrogen bonds as dashes lines).

## 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,  $P\bar{1}$

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<sup>3</sup>

$Z = 2$

$F_{000} = 344$

$D_x = 1.383$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 44 reflections

$\theta = 8.5\text{--}25.1^\circ$

$\mu = 0.73$  mm<sup>-1</sup>

$T = 173$  (2) K

Block, colorless

$0.40 \times 0.32 \times 0.30$  mm

### Data collection

Siemens P4 diffractometer

Radiation source: sealed tube

Monochromator: graphite

$T = 173$ (2) K

$2\theta/\omega$  scans

Absorption correction: none

4013 measured reflections

2967 independent reflections

2811 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.015$

$\theta_{max} = 25.5^\circ$

$\theta_{min} = 2.7^\circ$

$h = -6 \rightarrow 2$

$k = -11 \rightarrow 11$

$l = -18 \rightarrow 18$

3 standard reflections

every 197 reflections

intensity decay: none

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.128$	$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 0.5046P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
2967 reflections	$(\Delta/\sigma)_{\max} < 0.001$
175 parameters	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
2 restraints	$\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C14	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)
C11	0.70662 (8)	0.21020 (5)	0.44910 (3)	0.02735 (17)
C12	0.94353 (13)	0.32245 (6)	0.21628 (5)	0.0472 (2)
C13	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)

## supplementary materials

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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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C14	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)
C11	0.0176 (3)	0.0367 (3)	0.0265 (3)	0.0034 (2)	0.00211 (19)	0.0023 (2)
C12	0.0565 (4)	0.0326 (3)	0.0527 (4)	0.0009 (3)	0.0136 (3)	0.0079 (3)
C13	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 ( $\text{\AA}$ , $^\circ$ )

C14—C12	1.753 (2)	C11—H11A	0.9700
C12—C13	1.755 (2)	C11—H11B	0.9700
C12—C12	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)		
C14—C12—C13	111.93 (13)	C9—C8—H8A	109.6
C14—C12—C12	110.52 (13)	N1—C8—H8B	109.6
C13—C12—C12	110.17 (12)	C9—C8—H8B	109.6
C14—C12—H12	108.1 (19)	H8A—C8—H8B	108.2
C13—C12—H12	107.5 (19)	N2—C9—C8	110.19 (16)
C12—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)

## supplementary materials

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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 ( $\text{\AA}$ , $^\circ$ )

<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>
N2—H1N $\cdots$ C11	0.85 (2)	2.30 (2)	3.140 (2)	169 (2)
C12—H12 $\cdots$ C11	0.89 (3)	2.60 (3)	3.401 (2)	151 (2)
N2—H2N $\cdots$ C11 <sup>i</sup>	0.88 (2)	2.26 (2)	3.096 (2)	159 (2)
C10—H10A $\cdots$ C11 <sup>ii</sup>	0.97	2.74	3.684 (2)	165

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



Fig. 1

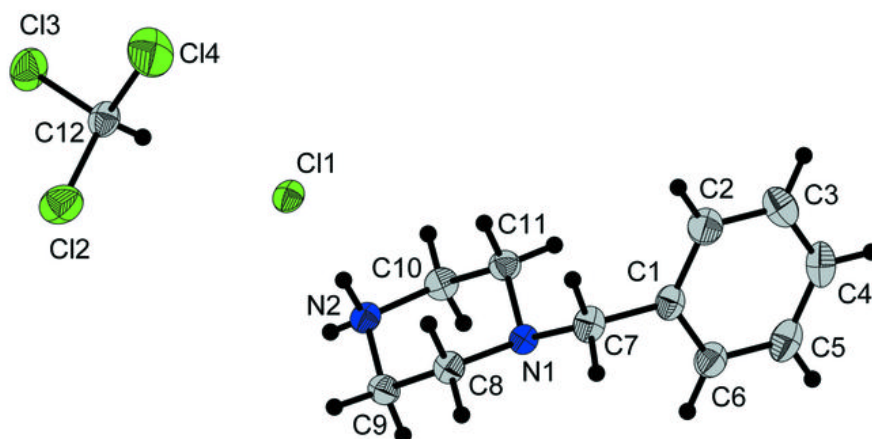


Fig. 2

