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# 4-(Methylsulfonyl)piperazin-1-ium chloride

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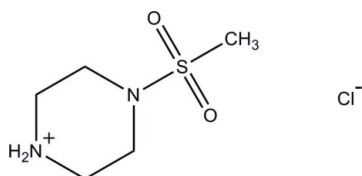
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.023;  $wR$  factor = 0.072; data-to-parameter ratio = 32.1.

In the title molecular salt,  $\text{C}_5\text{H}_{13}\text{N}_2\text{O}_2\text{S}^+\cdot\text{Cl}^-$ , the complete cation is generated by crystallographic mirror symmetry, with both N atoms, the S atom and one C atom lying on the reflecting plane. The chloride ion also lies on the mirror plane. The piperazinium ring adopts a chair conformation and the N—S bond adopts an equatorial orientation. In the crystal structure, the component ions are linked into a three-dimensional framework by intermolecular N—H $\cdots$ Cl and C—H $\cdots$ Cl hydrogen bonds.

## Related literature

For medicinal background to piperazine derivatives, see: Dinsmore & Beshore (2002); Berkheij *et al.* (2005); Humle & Cherrier (1999). For related structures, see: Bart *et al.* (1978); Girisha *et al.* (2008); Homrighausen & Krause Bauer (2002); Jin *et al.* (2007); Kubo *et al.* (2007); Parkin *et al.* (2004); Shen *et al.* (2006), Wang *et al.* (2006). For ring conformations, see: Cremer & Pople (1975). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



‡ Thomson Reuters ResearcherID: A-3561-2009.

§ Thomson Reuters ResearcherID: A-5523-2009.

## Experimental

## Crystal data

$\text{C}_5\text{H}_{13}\text{N}_2\text{O}_2\text{S}^+\cdot\text{Cl}^-$   
 $M_r = 200.68$   
 Monoclinic,  $P2_1/m$   
 $a = 6.0231$  (1) Å  
 $b = 9.1097$  (2) Å  
 $c = 7.9852$  (2) Å  
 $\beta = 100.700$  (1)°  
 $V = 430.52$  (2) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.64$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.36 \times 0.32 \times 0.05$  mm

## Data collection

Bruker APEX Duo CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2009)  
 $T_{\min} = 0.801$ ,  $T_{\max} = 0.968$   
 10626 measured reflections  
 2790 independent reflections  
 2419 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.072$   
 $S = 1.10$   
 2790 reflections  
 87 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.49$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.40$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                                      | $D-H$      | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------------------------|------------|-------------|-------------|---------------|
| $\text{N1}-\text{H1N1}\cdots\text{Cl}^{\text{i}}$  | 0.92 (2)   | 2.40 (2)    | 3.1341 (8)  | 137 (1)       |
| $\text{N1}-\text{H2N1}\cdots\text{Cl}^{\text{ii}}$ | 0.93 (2)   | 2.19 (2)    | 3.0966 (8)  | 164 (1)       |
| $\text{C1}-\text{H1A}\cdots\text{Cl}^{\text{iii}}$ | 0.953 (12) | 2.700 (12)  | 3.5251 (6)  | 145.2 (9)     |
| $\text{C3}-\text{H3A}\cdots\text{Cl}^{\text{i}}$   | 0.94 (2)   | 2.65 (2)    | 3.5487 (10) | 160 (2)       |

Symmetry codes: (i)  $x + 1, y, z - 1$ ; (ii)  $x, y, z - 1$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z + 1$ .

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5306).

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## supporting information

*Acta Cryst.* (2010). E66, o361–o362 [https://doi.org/10.1107/S1600536810001224]

**4-(Methylsulfonyl)piperazin-1-ium chloride**

**Hoong-Kun Fun, Chin Sing Yeap, C. S. Chidan Kumar, H. S. Yathirajan and B. Narayana**

**S1. Comment**

Piperazines are among the most important building blocks in today's drug discovery. The piperazine nucleus is capable of binding to multiple receptors with high affinity and therefore piperazine has been classified as a privileged structure (Dinsmore & Beshore, 2002). They are found in biologically active compounds across a number of different therapeutic areas (Berkheij *et al.*, 2005) such as antifungal, antibacterial, antimalarial, antipsychotic, antidepressant and antitumour activity against colon, prostate, breast, lung and leukemia tumors (Humle & Cherrier, 1999). The piperazines are a broad class of chemical compounds, many with important pharmacological properties, which contain a core piperazine functional group. 1-(Methylsulfonyl)piperazine is an important intermediate in synthetic organic chemistry, mainly used as a pharmaceutical intermediate.

The crystal structures of *trans*-2,5-dimethylpiperazine dihydrochloride (Bart *et al.*, 1978), 1-(3-chlorophenyl)-4-(3-chloropropyl)piperazinium chloride (Homrighausen & Krause Bauer, 2002), piperazine (Parkin *et al.*, 2004), 2,2'-(piperazine-1,4-dium-1,4-diyl)diacetate dehydrate (Shen *et al.*, 2006), 1,4-bis(chloroacetyl)piperazine (Wang *et al.*, 2006), 1,4-bis(1-naphthylmethyl) piperazine (Kubo *et al.*, 2007), 1,4-bis(4-chlorobenzo-yl)piperazine (Jin *et al.*, 2007) and 1-benzhydryl-4-(4-chlorophenylsulfonyl) piperazine (Girisha *et al.*, 2008) have been reported. In view of the importance of the title compound, this paper reports its crystal structure.

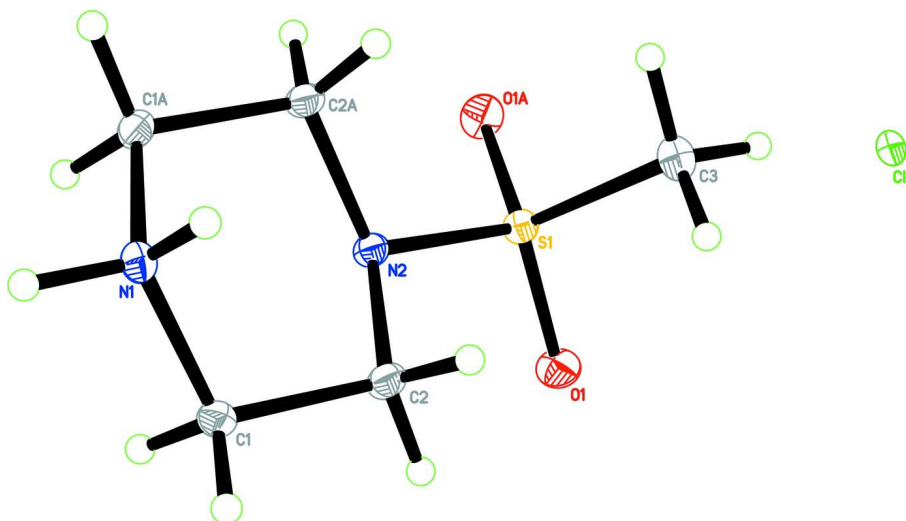
The asymmetric unit of the title compound contains one-half of a cation and half of a chloride anion (Fig. 1). The C11, S1, N1, N2, and C3 atoms are lying on a mirror plane. The piperazinium ring adopts a chair conformation with puckering amplitude  $Q = 0.5680(7) \text{ \AA}$ ,  $\theta = 179.90(7)^\circ$ ,  $\varphi = 180(7)^\circ$  (Cremer & Pople, 1975). In the crystal structure (Fig. 2), the molecules are linked into a three-dimensional framework by intermolecular hydrogen bonds (Table 1).

**S2. Experimental**

The title compound was obtained as a gift sample from *R. L. Fine Chem.*, Bangalore, India. The compound was used without further purification. Colourless plates of (I) were obtained from slow evaporation of a methanol solution (m.p.: 489–492 K).

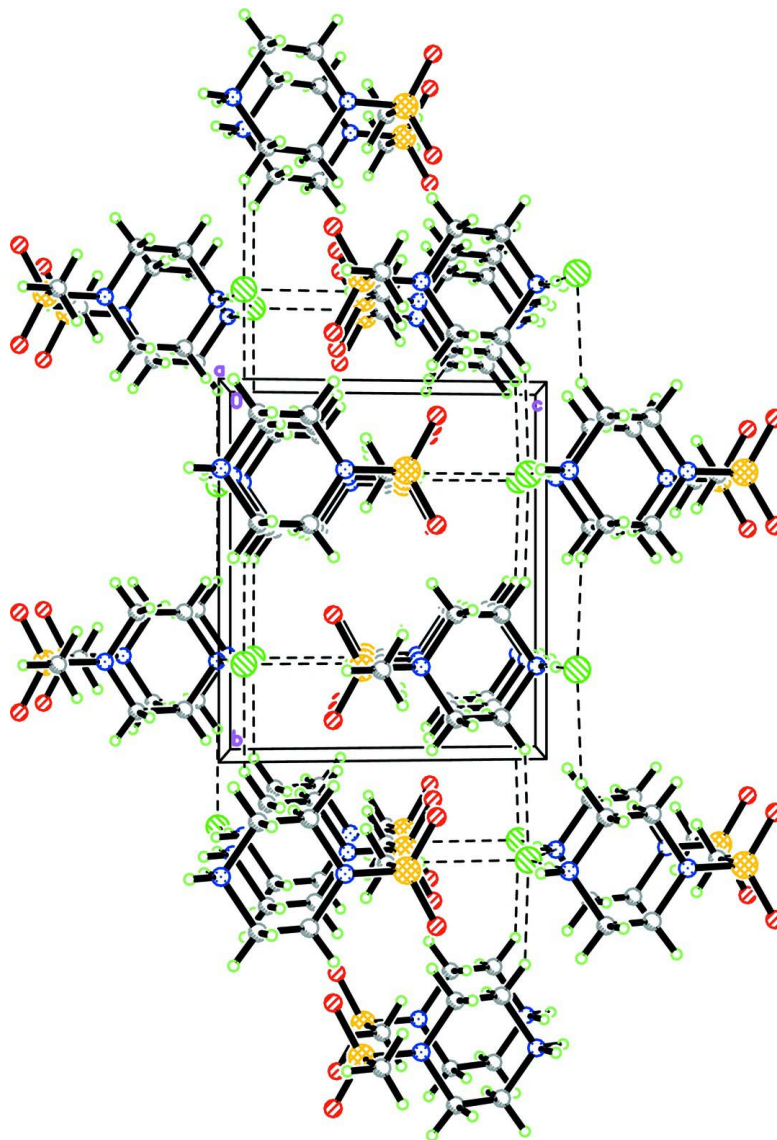
**S3. Refinement**

All H atoms were located in a difference Fourier map and refined freely.



**Figure 1**

The molecular structure of (I) with 50% probability ellipsoids for the non-H atoms. Atoms with suffix A are generated by the symmetry operation  $(x, 1/2 - y, z)$ .



**Figure 2**

The crystal packing of (I), viewed down the  $a$  axis, showing the hydrogen-bonded (dashed lines) three-dimensional framework.

#### 4-(Methylsulfonyl)piperazin-1-ium chloride

##### Crystal data

$C_5H_{13}N_2O_2S^+Cl^-$

$M_r = 200.68$

Monoclinic,  $P2_1/m$

Hall symbol:  $-P\ 2yb$

$a = 6.0231$  (1) Å

$b = 9.1097$  (2) Å

$c = 7.9852$  (2) Å

$\beta = 100.700$  (1)°

$V = 430.52$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 212$

$D_x = 1.548$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4890 reflections

$\theta = 3.4\text{--}40.1^\circ$

$\mu = 0.64$  mm<sup>-1</sup>

$T = 100$  K

Plate, colourless

$0.36 \times 0.32 \times 0.05$  mm

*Data collection*

Bruker APEX Duo CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.801$ ,  $T_{\max} = 0.968$

10626 measured reflections

2790 independent reflections

2419 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 40.1^\circ$ ,  $\theta_{\min} = 2.6^\circ$

$h = -10 \rightarrow 10$

$k = -14 \rightarrow 16$

$l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.072$

$S = 1.10$

2790 reflections

87 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 atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.0922P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

*Special details*

**Experimental.** The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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

|     | <i>x</i>     | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| C11 | 0.30674 (3)  | 0.2500      | 0.93448 (3)  | 0.01195 (5)                      |
| S1  | 0.69091 (3)  | 0.2500      | 0.56598 (2)  | 0.00951 (5)                      |
| N1  | 0.82854 (12) | 0.2500      | 0.03611 (9)  | 0.01007 (11)                     |
| N2  | 0.79320 (12) | 0.2500      | 0.38830 (9)  | 0.00974 (11)                     |
| O1  | 0.75935 (9)  | 0.11396 (6) | 0.65235 (6)  | 0.01498 (9)                      |
| C1  | 0.87784 (10) | 0.11522 (7) | 0.14202 (8)  | 0.01165 (9)                      |
| C2  | 0.74465 (10) | 0.11465 (7) | 0.28537 (8)  | 0.01168 (9)                      |
| C3  | 0.39411 (15) | 0.2500      | 0.50705 (12) | 0.01332 (13)                     |
| H1A | 0.8351 (18)  | 0.0315 (13) | 0.0719 (14)  | 0.012 (2)*                       |
| H1B | 1.040 (2)    | 0.1186 (13) | 0.1845 (16)  | 0.016 (3)*                       |
| H2A | 0.583 (2)    | 0.1017 (14) | 0.2371 (15)  | 0.018 (3)*                       |
| H2B | 0.789 (2)    | 0.0335 (16) | 0.3554 (17)  | 0.027 (3)*                       |
| H3A | 0.331 (3)    | 0.2500      | 0.606 (2)    | 0.019 (4)*                       |
| H3B | 0.350 (2)    | 0.3381 (15) | 0.4460 (16)  | 0.025 (3)*                       |

|      |           |        |            |            |
|------|-----------|--------|------------|------------|
| H1N1 | 0.914 (3) | 0.2500 | -0.048 (2) | 0.019 (4)* |
| H2N1 | 0.677 (3) | 0.2500 | -0.017 (2) | 0.021 (4)* |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| C11 | 0.00886 (7)  | 0.01261 (8)  | 0.01485 (9)  | 0.000         | 0.00346 (6)  | 0.000         |
| S1  | 0.01110 (8)  | 0.01033 (8)  | 0.00696 (8)  | 0.000         | 0.00128 (6)  | 0.000         |
| N1  | 0.0098 (2)   | 0.0115 (3)   | 0.0095 (3)   | 0.000         | 0.00316 (19) | 0.000         |
| N2  | 0.0126 (2)   | 0.0084 (2)   | 0.0087 (2)   | 0.000         | 0.0032 (2)   | 0.000         |
| O1  | 0.01874 (19) | 0.01499 (19) | 0.01109 (18) | 0.00356 (16)  | 0.00245 (15) | 0.00480 (15)  |
| C1  | 0.0148 (2)   | 0.00900 (19) | 0.0122 (2)   | 0.00097 (17)  | 0.00547 (17) | -0.00041 (17) |
| C2  | 0.0162 (2)   | 0.0083 (2)   | 0.0117 (2)   | -0.00109 (16) | 0.00571 (17) | -0.00060 (16) |
| C3  | 0.0115 (3)   | 0.0166 (3)   | 0.0121 (3)   | 0.000         | 0.0027 (2)   | 0.000         |

*Geometric parameters (Å, °)*

|                           |            |                           |            |
|---------------------------|------------|---------------------------|------------|
| S1—O1 <sup>i</sup>        | 1.4408 (5) | N2—C2 <sup>i</sup>        | 1.4806 (7) |
| S1—O1                     | 1.4408 (5) | C1—C2                     | 1.5148 (8) |
| S1—N2                     | 1.6484 (7) | C1—H1A                    | 0.953 (11) |
| S1—C3                     | 1.7621 (9) | C1—H1B                    | 0.976 (12) |
| N1—C1                     | 1.4892 (7) | C2—H2A                    | 0.983 (13) |
| N1—C1 <sup>i</sup>        | 1.4892 (7) | C2—H2B                    | 0.935 (14) |
| N1—H1N1                   | 0.920 (17) | C3—H3A                    | 0.941 (18) |
| N1—H2N1                   | 0.933 (19) | C3—H3B                    | 0.951 (14) |
| N2—C2                     | 1.4806 (7) |                           |            |
| O1 <sup>i</sup> —S1—O1    | 118.67 (4) | N1—C1—C2                  | 110.75 (5) |
| O1 <sup>i</sup> —S1—N2    | 107.01 (2) | N1—C1—H1A                 | 108.8 (7)  |
| O1—S1—N2                  | 107.01 (2) | C2—C1—H1A                 | 108.5 (6)  |
| O1 <sup>i</sup> —S1—C3    | 108.28 (3) | N1—C1—H1B                 | 104.6 (7)  |
| O1—S1—C3                  | 108.29 (3) | C2—C1—H1B                 | 112.1 (7)  |
| N2—S1—C3                  | 107.03 (4) | H1A—C1—H1B                | 112.0 (9)  |
| C1—N1—C1 <sup>i</sup>     | 111.07 (7) | N2—C2—C1                  | 109.81 (5) |
| C1—N1—H1N1                | 109.7 (5)  | N2—C2—H2A                 | 113.4 (7)  |
| C1 <sup>i</sup> —N1—H1N1  | 109.7 (5)  | C1—C2—H2A                 | 109.1 (7)  |
| C1—N1—H2N1                | 109.5 (5)  | N2—C2—H2B                 | 108.7 (8)  |
| C1 <sup>i</sup> —N1—H2N1  | 109.5 (5)  | C1—C2—H2B                 | 108.7 (7)  |
| H1N1—N1—H2N1              | 107.3 (15) | H2A—C2—H2B                | 107.1 (10) |
| C2—N2—C2 <sup>i</sup>     | 112.77 (7) | S1—C3—H3A                 | 108.9 (11) |
| C2—N2—S1                  | 114.27 (4) | S1—C3—H3B                 | 108.1 (8)  |
| C2 <sup>i</sup> —N2—S1    | 114.27 (4) | H3A—C3—H3B                | 108.3 (9)  |
| O1 <sup>i</sup> —S1—N2—C2 | 178.10 (5) | C3—S1—N2—C2 <sup>i</sup>  | 66.00 (5)  |
| O1—S1—N2—C2               | 49.91 (6)  | C1 <sup>i</sup> —N1—C1—C2 | 56.95 (8)  |
| C3—S1—N2—C2               | -65.99 (5) | C2 <sup>i</sup> —N2—C2—C1 | 56.73 (8)  |

|                                        |             |             |             |
|----------------------------------------|-------------|-------------|-------------|
| O1 <sup>i</sup> —S1—N2—C2 <sup>i</sup> | -49.91 (6)  | S1—N2—C2—C1 | -170.56 (4) |
| O1—S1—N2—C2 <sup>i</sup>               | -178.10 (5) | N1—C1—C2—N2 | -55.89 (7)  |

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

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i>               | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|------------------------------|------------|--------------|--------------|----------------|
| N1—H1M1...C11 <sup>ii</sup>  | 0.92 (2)   | 2.40 (2)     | 3.1341 (8)   | 137 (1)        |
| N1—H2M1...C11 <sup>iii</sup> | 0.93 (2)   | 2.19 (2)     | 3.0966 (8)   | 164 (1)        |
| C1—H1A...C11 <sup>iv</sup>   | 0.953 (12) | 2.700 (12)   | 3.5251 (6)   | 145.2 (9)      |
| C3—H3A...C11                 | 0.94 (2)   | 2.65 (2)     | 3.5487 (10)  | 160 (2)        |

Symmetry codes: (ii)  $x+1, y, z-1$ ; (iii)  $x, y, z-1$ ; (iv)  $-x+1, y-1/2, -z+1$ .