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2,2′-[*o*-Phenylenebis(methylenethio)]-bis(pyridine *N*-oxide)

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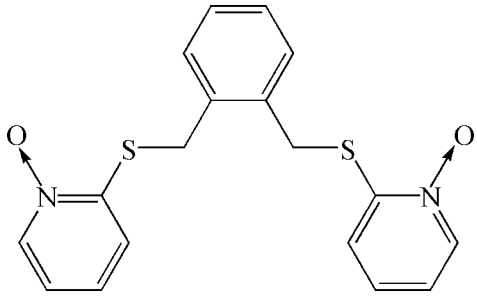
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.083; data-to-parameter ratio = 16.8.

In the title compound, $C_{18}H_{16}N_2O_2S_2$, the benzene ring makes dihedral angles of 7.41 and 86.59° with the two outer pyridine N-oxygen rings. Two short intramolecular C—H···S contacts occur. The crystal packing is stabilized by C—H···O hydrogen bonds, C—H···π interactions and weak π–π staking interactions [centroid–centroid distance 3.7596 (7) Å].

Related literature

For a related stucture, see: Han *et al.* (2005). For thioether compounds, see: Xie *et al.* (2005).



Experimental

Crystal data

$C_{18}H_{16}N_2O_2S_2$
M_r = 356.47
Monoclinic, $P2_1/n$
a = 7.5075 (15) Å
b = 17.810 (4) Å
c = 12.480 (3) Å
β = 105.20 (3)°
V = 1610.3 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 293 K
0.34 × 0.28 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
9681 measured reflections
3782 independent reflections
3145 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.02
3782 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.25 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
C2—H2A···O1^{i}	0.93	2.42	3.133 (2)	134
C5—H5A···O1^{ii}	0.93	2.38	3.253 (2)	155
C8—H8A···S1	0.93	2.67	3.1105 (18)	110
C11—H11A···S2	0.93	2.47	2.9322 (18)	111
C15—H15A···O2^{iii}	0.93	2.58	3.461 (2)	158
C9—H9A···$Cg2^{iv}$	0.93	2.90	3.645 (2)	138

Symmetry codes: (i) $-x-1, -y, -z$; (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x, -y, -z+1$. $Cg2$ is the centroid of the N2/C1–C5 ring.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); 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, 2008); 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: AT2798).

References

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supporting information

Acta Cryst. (2009). E**65**, o1482 [doi:10.1107/S160053680902073X]

2,2′-[*o*-Phenylenebis(methylenethio)]bis(pyridine *N*-oxide)

Chao-Yan Zhang, Qian Gao, Yue Cui and Ya-Bo Xie

S1. Comment

Thioether-type ligands are attracting great attention as the conformational freedom, flexible multidentate bridging ligands (Xie *et al.*, 2005). In continuation of the structural study of thioether-type ligands (Han *et al.*, 2005), herein, we report the crystal sructure of the title compound.

The title compound (Fig. 1) was obtained by the reaction of 2-mercaptopyridine N-oxide and *o*-xylylene dibromide. In the asymmetric unit, the central benzene ring makes dihedral angles of 7.44 and 86.52° with the two outer pyridine N-oxygen rings and the crystal packing is stabilized by C—H···O and C—H..S hydrogen bonding, C—H···π interactions (Table 1) and weak π-π staking interactions [centroid-to-centroid distance 3.7596 (7) Å].

S2. Experimental

2-Mercaptopyridine N-oxide (1.2719 g, 10.00 mmol) was added to a stirred solution of KOH (0.6091 g, 10.85 mmol) in ethanol (50 ml). After 30 min, *o*-xylylene dibromide (1.3206 g, 5.00 mmol) was added and the mixture was heated to 343 K for 6 h with vigorous stirring. The mixture was cooled to room temperature and the precipitate was filtered off and washed with ethanol and water, giving a white powder in 66.0% yield. Then, a solution of the powder in $CHCl_3$/CH_3CN with a molar ratio of 1:1 was filtered. Slow diffusion of ether into the filtrate yielded colourless prism crystals.

S3. Refinement

The H atoms H6A and H6B of the C6 atom were found from a difference Fourier map and refined freely. The rest H atoms were fixed geometrically with C—H = 0.93-0.97 Å and treated as riding with U_{iso}(H) = 1.2U_{eq}(C).

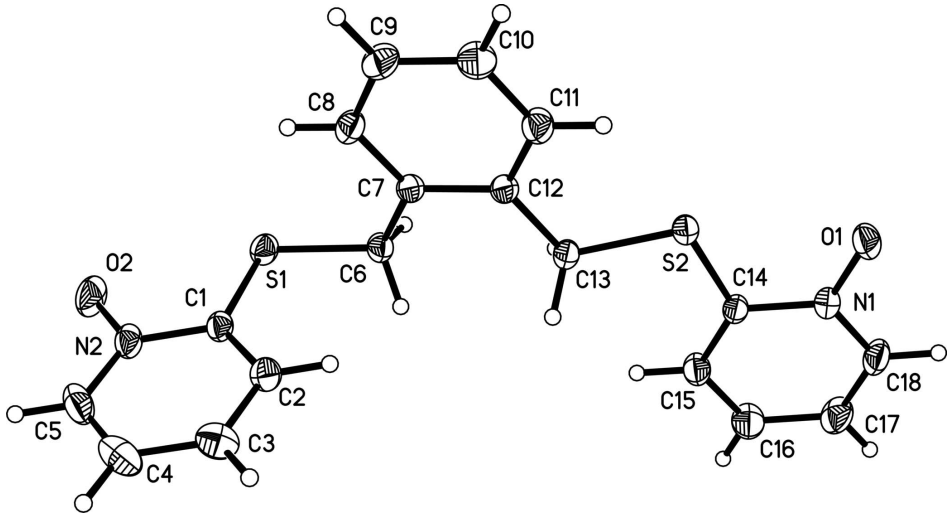

Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level for non-hydrogen atoms.

2,2′-[*o*-Phenylenebis(methylenethio)]bis(pyridine *N*-oxide)

Crystal data

$C_{18}H_{16}N_2O_2S_2$
$M_r = 356.47$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.5075\ (15)$ Å
$b = 17.810\ (4)$ Å
$c = 12.480\ (3)$ Å
$\beta = 105.20\ (3)°$
$V = 1610.3\ (7)$ Å^3
$Z = 4$
$F(000) = 744$
$D_x = 1.470$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9866 reflections
$\theta = 2.0–27.9°$
$\mu = 0.34$ mm^{-1}
$T = 293$ K
Prism, colourless
0.34 × 0.28 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
9681 measured reflections
3782 independent reflections
3145 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 27.9°$, $\theta_{min} = 2.0°$
$h = -8\rightarrow9$
$k = -17\rightarrow23$
$l = -15\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.083$
$S = 1.02$
3782 reflections
225 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

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.5053P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ 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}
S1	0.17377 (5)	0.17901 (2)	0.34399 (3)	0.03675 (11)
S2	−0.30419 (5)	−0.03050 (2)	−0.04963 (3)	0.03289 (10)
C7	−0.00609 (19)	0.04497 (8)	0.25080 (11)	0.0304 (3)
N1	−0.47078 (17)	−0.01887 (7)	−0.25627 (10)	0.0350 (3)
O1	−0.48428 (16)	−0.09127 (6)	−0.24087 (9)	0.0458 (3)
C14	−0.38096 (18)	0.02425 (8)	−0.16810 (11)	0.0308 (3)
C6	0.0423 (2)	0.12465 (8)	0.22786 (12)	0.0335 (3)
C1	0.0008 (2)	0.20710 (8)	0.40531 (11)	0.0324 (3)
C12	−0.11785 (18)	0.00251 (8)	0.16387 (11)	0.0301 (3)
C15	−0.3632 (2)	0.10057 (9)	−0.18273 (13)	0.0397 (3)
H15A	−0.3009	0.1304	−0.1235	0.048*
N2	0.06622 (19)	0.25129 (7)	0.49662 (10)	0.0402 (3)
C2	−0.1847 (2)	0.18976 (9)	0.37257 (13)	0.0388 (3)
H2A	−0.2299	0.1592	0.3111	0.047*
C11	−0.1519 (2)	−0.07213 (9)	0.18381 (13)	0.0421 (4)
H11A	−0.2260	−0.1007	0.1270	0.051*
C13	−0.19734 (19)	0.03928 (8)	0.05228 (11)	0.0318 (3)
H13A	−0.0999	0.0646	0.0285	0.038*
H13B	−0.2883	0.0765	0.0587	0.038*
O2	0.24350 (18)	0.26652 (7)	0.52668 (10)	0.0570 (3)
C8	0.0643 (2)	0.01115 (9)	0.35310 (12)	0.0402 (3)
H8A	0.1367	0.0392	0.4112	0.048*
C9	0.0293 (3)	−0.06342 (10)	0.37091 (14)	0.0500 (4)
H9A	0.0787	−0.0852	0.4401	0.060*
C18	−0.5444 (2)	0.01241 (10)	−0.35676 (13)	0.0456 (4)
H18A	−0.6060	−0.0178	−0.4157	0.055*
C5	−0.0505 (3)	0.27874 (9)	0.55340 (14)	0.0536 (5)
H5A	−0.0048	0.3091	0.6151	0.064*
C3	−0.3033 (3)	0.21749 (10)	0.43040 (16)	0.0511 (4)
H3A	−0.4284	0.2060	0.4084	0.061*
C17	−0.5296 (3)	0.08746 (11)	−0.37289 (14)	0.0527 (4)
H17A	−0.5807	0.1085	−0.4424	0.063*

C16	−0.4379 (3)	0.13227 (10)	−0.28521 (14)	0.0507 (4)
H16A	−0.4269	0.1836	−0.2955	0.061*
C10	−0.0783 (3)	−0.10491 (10)	0.28622 (14)	0.0512 (4)
H10A	−0.1019	−0.1552	0.2975	0.061*
C4	−0.2338 (3)	0.26248 (10)	0.52122 (17)	0.0584 (5)
H4A	−0.3125	0.2819	0.5608	0.070*
H6A	0.125 (2)	0.1237 (9)	0.1798 (14)	0.042 (4)*
H6B	−0.062 (2)	0.1528 (10)	0.1903 (14)	0.043 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.03174 (19)	0.0384 (2)	0.0364 (2)	−0.00423 (14)	0.00247 (14)	−0.00293 (15)
S2	0.03698 (19)	0.03129 (19)	0.02808 (18)	0.00011 (14)	0.00442 (14)	−0.00330 (13)
C7	0.0319 (7)	0.0324 (7)	0.0271 (7)	0.0032 (5)	0.0081 (5)	−0.0001 (5)
N1	0.0348 (6)	0.0363 (7)	0.0308 (6)	−0.0028 (5)	0.0034 (5)	−0.0047 (5)
O1	0.0547 (7)	0.0324 (6)	0.0443 (6)	−0.0074 (5)	0.0022 (5)	−0.0070 (5)
C14	0.0285 (7)	0.0351 (7)	0.0271 (7)	−0.0009 (5)	0.0044 (5)	−0.0038 (5)
C6	0.0403 (8)	0.0321 (7)	0.0267 (7)	0.0001 (6)	0.0064 (6)	−0.0010 (5)
C1	0.0395 (8)	0.0268 (7)	0.0277 (7)	−0.0026 (6)	0.0033 (6)	−0.0006 (5)
C12	0.0308 (7)	0.0320 (7)	0.0276 (7)	0.0021 (5)	0.0078 (5)	−0.0003 (5)
C15	0.0450 (9)	0.0357 (8)	0.0354 (8)	−0.0046 (6)	0.0054 (6)	−0.0039 (6)
N2	0.0555 (8)	0.0280 (6)	0.0312 (6)	−0.0053 (6)	0.0009 (6)	−0.0017 (5)
C2	0.0385 (8)	0.0371 (8)	0.0390 (8)	−0.0029 (6)	0.0069 (6)	−0.0036 (6)
C11	0.0507 (9)	0.0357 (8)	0.0365 (8)	−0.0049 (7)	0.0053 (7)	0.0004 (6)
C13	0.0333 (7)	0.0323 (7)	0.0271 (7)	−0.0009 (5)	0.0031 (5)	−0.0019 (5)
O2	0.0580 (8)	0.0494 (7)	0.0497 (7)	−0.0150 (6)	−0.0107 (6)	−0.0095 (6)
C8	0.0462 (9)	0.0415 (8)	0.0283 (7)	0.0008 (7)	0.0015 (6)	0.0019 (6)
C9	0.0655 (11)	0.0444 (9)	0.0351 (9)	0.0038 (8)	0.0046 (8)	0.0130 (7)
C18	0.0472 (9)	0.0530 (10)	0.0289 (8)	−0.0032 (8)	−0.0037 (6)	−0.0035 (7)
C5	0.0920 (15)	0.0324 (8)	0.0374 (9)	0.0016 (9)	0.0186 (9)	−0.0065 (7)
C3	0.0484 (10)	0.0446 (9)	0.0644 (12)	0.0024 (8)	0.0223 (9)	0.0019 (8)
C17	0.0617 (11)	0.0541 (11)	0.0348 (9)	−0.0003 (9)	−0.0004 (7)	0.0086 (7)
C16	0.0653 (11)	0.0380 (9)	0.0447 (10)	−0.0039 (8)	0.0071 (8)	0.0055 (7)
C10	0.0695 (12)	0.0348 (8)	0.0467 (10)	−0.0019 (8)	0.0104 (8)	0.0093 (7)
C4	0.0828 (14)	0.0410 (10)	0.0630 (12)	0.0088 (9)	0.0398 (11)	−0.0010 (8)

Geometric parameters (Å, º)

S1—C1	1.7442 (15)	C2—C3	1.376 (2)
S1—C6	1.8061 (15)	C2—H2A	0.9300
S2—C14	1.7384 (15)	C11—C10	1.382 (2)
S2—C13	1.8084 (14)	C11—H11A	0.9300
C7—C8	1.385 (2)	C13—H13A	0.9700
C7—C12	1.4055 (19)	C13—H13B	0.9700
C7—C6	1.511 (2)	C8—C9	1.383 (2)
N1—O1	1.3116 (16)	C8—H8A	0.9300
N1—C18	1.351 (2)	C9—C10	1.367 (2)

N1—C14	1.3660 (17)	C9—H9A	0.9300
C14—C15	1.383 (2)	C18—C17	1.361 (3)
C6—H6A	0.971 (17)	C18—H18A	0.9300
C6—H6B	0.942 (18)	C5—C4	1.360 (3)
C1—N2	1.3658 (18)	C5—H5A	0.9300
C1—C2	1.380 (2)	C3—C4	1.374 (3)
C12—C11	1.389 (2)	C3—H3A	0.9300
C12—C13	1.5128 (19)	C17—C16	1.383 (2)
C15—C16	1.376 (2)	C17—H17A	0.9300
C15—H15A	0.9300	C16—H16A	0.9300
N2—O2	1.3130 (18)	C10—H10A	0.9300
N2—C5	1.355 (2)	C4—H4A	0.9300

C1—S1—C6	101.12 (7)	C12—C11—H11A	119.3
C14—S2—C13	101.52 (7)	C12—C13—S2	110.19 (10)
C8—C7—C12	118.93 (13)	C12—C13—H13A	109.6
C8—C7—C6	122.05 (13)	S2—C13—H13A	109.6
C12—C7—C6	118.93 (12)	C12—C13—H13B	109.6
O1—N1—C18	120.85 (12)	S2—C13—H13B	109.6
O1—N1—C14	118.39 (12)	H13A—C13—H13B	108.1
C18—N1—C14	120.76 (13)	C9—C8—C7	121.54 (14)
N1—C14—C15	119.39 (13)	C9—C8—H8A	119.2
N1—C14—S2	110.69 (10)	C7—C8—H8A	119.2
C15—C14—S2	129.92 (11)	C10—C9—C8	119.57 (15)
C7—C6—S1	117.35 (10)	C10—C9—H9A	120.2
C7—C6—H6A	109.0 (10)	C8—C9—H9A	120.2
S1—C6—H6A	101.6 (10)	N1—C18—C17	120.86 (15)
C7—C6—H6B	112.7 (10)	N1—C18—H18A	119.6
S1—C6—H6B	108.7 (10)	C17—C18—H18A	119.6
H6A—C6—H6B	106.4 (14)	N2—C5—C4	120.81 (16)
N2—C1—C2	119.34 (14)	N2—C5—H5A	119.6
N2—C1—S1	112.67 (11)	C4—C5—H5A	119.6
C2—C1—S1	127.99 (12)	C4—C3—C2	118.96 (17)
C11—C12—C7	118.52 (13)	C4—C3—H3A	120.5
C11—C12—C13	122.19 (13)	C2—C3—H3A	120.5
C7—C12—C13	119.29 (12)	C18—C17—C16	119.52 (16)
C16—C15—C14	119.74 (14)	C18—C17—H17A	120.2
C16—C15—H15A	120.1	C16—C17—H17A	120.2
C14—C15—H15A	120.1	C15—C16—C17	119.72 (16)
O2—N2—C5	121.49 (14)	C15—C16—H16A	120.1
O2—N2—C1	118.23 (13)	C17—C16—H16A	120.1
C5—N2—C1	120.27 (14)	C9—C10—C11	119.92 (15)
C3—C2—C1	120.38 (15)	C9—C10—H10A	120.0
C3—C2—H2A	119.8	C11—C10—H10A	120.0
C1—C2—H2A	119.8	C5—C4—C3	120.23 (17)
C10—C11—C12	121.50 (15)	C5—C4—H4A	119.9
C10—C11—H11A	119.3	C3—C4—H4A	119.9

O1—N1—C14—C15	179.24 (13)	S1—C1—C2—C3	−179.40 (13)
C18—N1—C14—C15	−1.0 (2)	C7—C12—C11—C10	−0.2 (2)
O1—N1—C14—S2	−0.70 (16)	C13—C12—C11—C10	180.00 (15)
C18—N1—C14—S2	179.09 (12)	C11—C12—C13—S2	−9.11 (17)
C13—S2—C14—N1	−178.90 (10)	C7—C12—C13—S2	171.08 (10)
C13—S2—C14—C15	1.17 (16)	C14—S2—C13—C12	−179.41 (9)
C8—C7—C6—S1	−7.41 (19)	C12—C7—C8—C9	1.0 (2)
C12—C7—C6—S1	176.13 (10)	C6—C7—C8—C9	−175.47 (15)
C1—S1—C6—C7	−80.37 (12)	C7—C8—C9—C10	−0.5 (3)
C6—S1—C1—N2	−178.97 (10)	O1—N1—C18—C17	−179.67 (16)
C6—S1—C1—C2	1.27 (15)	C14—N1—C18—C17	0.5 (2)
C8—C7—C12—C11	−0.6 (2)	O2—N2—C5—C4	179.98 (16)
C6—C7—C12—C11	175.95 (13)	C1—N2—C5—C4	0.5 (2)
C8—C7—C12—C13	179.20 (13)	C1—C2—C3—C4	−0.1 (3)
C6—C7—C12—C13	−4.23 (19)	N1—C18—C17—C16	0.0 (3)
N1—C14—C15—C16	0.8 (2)	C14—C15—C16—C17	−0.3 (3)
S2—C14—C15—C16	−179.24 (13)	C18—C17—C16—C15	−0.1 (3)
C2—C1—N2—O2	179.46 (13)	C8—C9—C10—C11	−0.3 (3)
S1—C1—N2—O2	−0.33 (17)	C12—C11—C10—C9	0.7 (3)
C2—C1—N2—C5	−1.0 (2)	N2—C5—C4—C3	0.2 (3)
S1—C1—N2—C5	179.20 (12)	C2—C3—C4—C5	−0.4 (3)
N2—C1—C2—C3	0.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O1^{i}	0.93	2.42	3.133 (2)	134
C5—H5*A*···O1^{ii}	0.93	2.38	3.253 (2)	155
C8—H8*A*···S1	0.93	2.67	3.1105 (18)	110
C11—H11*A*···S2	0.93	2.47	2.9322 (18)	111
C15—H15*A*···O2^{iii}	0.93	2.58	3.461 (2)	158
C9—H9*A*···*Cg*2^{iv}	0.93	2.90	3.645 (2)	138

Symmetry codes: (i) −*x*−1, −*y*, −*z*; (ii) −*x*−1/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+1/2, *z*−1/2; (iv) −*x*, −*y*, −*z*+1.