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Crystal structure of (4Z)-4-[(dimethyl-amino)methylidene]-3,5-dioxo-2-phenyl-pyrazolidine-1-carbaldehyde

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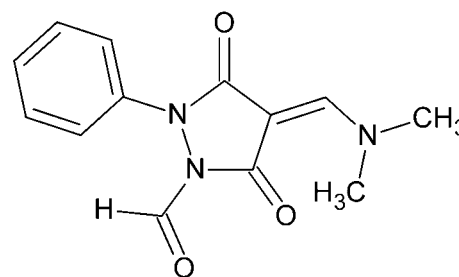
In the title compound, $C_{13}H_{13}N_3O_3$, the pyrazolidine ring adopts a shallow envelope conformation, with the carbonyl C atom closest to the benzene ring as the flap [deviation of 0.126 (1) Å from the plane through the remaining atoms (r.m.s. deviation = 0.011 Å)]. The dihedral angle between the pyrazolidine ring (all atoms) and the benzene ring is 51.09 (4)°. An extremely short (2.08 Å) intramolecular C—H⋯O contact is seen. In the crystal, molecules are linked by C—H⋯O bonds, generating [010] chains. Extremely weak C—H⋯π interactions are also observed.

1. Related literature

For biological studies of azole compounds, see: Patel et al. (2012); Vijesh et al. (2011). For various medicinal and industrial applications of pyrrazole-containing compounds, see: Jin et al. (2011); Zhang et al. (2010); El-Sabbagh et al. (2009); Dekhane et al. (2011); Rostom et al. (2003); Zhou et al. (2010); Finkelstein & Strock (1997).

2. Experimental

2.1. Crystal data

$C_{13}H_{13}N_3O_3$	$V = 2497.96$ (15) Å³
$M_r = 259.26$	$Z = 8$
Monoclinic, $C2/c$	Cu $K\alpha$ radiation
$a = 26.4235$ (9) Å	$\mu = 0.84$ mm⁻¹
$b = 6.1033$ (2) Å	$T = 150$ K
$c = 16.8611$ (6) Å	$0.24 \times 0.15 \times 0.05$ mm
$\beta = 113.272$ (1)°	

2.2. Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer	26486 measured reflections
Absorption correction: multi-scan (TWINABS; Sheldrick, 2009)	4565 independent reflections
$T_{min} = 0.82$, $T_{max} = 0.96$	3979 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	175 parameters
$wR(F^2) = 0.104$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.26$ e Å⁻³
4565 reflections	$\Delta\rho_{min} = -0.20$ e Å⁻³

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

Cg1 is the centroid of the C1/C2/C3/N1/N2 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6A⋯O2	0.98	2.08	3.016 (2)	160
C5—H5C⋯O3[i]	0.98	2.52	3.1803 (19)	124
C7—H7⋯O2[ii]	0.95	2.29	3.0663 (16)	139
C5—H5B⋯Cg1[iii]	0.98	2.98	3.8823 (18)	153

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

Data collection: APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT; program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 2012); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Crystal structure of (4*Z*)-4-[(dimethylamino)methylidene]-3,5-dioxo-2-phenyl-pyrazolidine-1-carbaldehyde

Joel T. Mague, Shaaban K. Mohamed, Mehmet Akkurt, Eman A. Ahmed and Ahmed Khodairy

S1. Comment

Azole compounds are extensively studied and widely used as anti-microbial agents (Patel *et al.*, 2012; Vijesh *et al.*, 2011). Recently, urea derivatives of pyrazole have been reported as potent inhibitors of p38 kinase (Jin *et al.*, 2011). Many of other pyrazole scaffold compounds are reported to have broad spectra of biological activities, such as anti-fungal (Zhang *et al.*, 2010), anti-viral (El-Sabbagh *et al.*, 2009), anti-inflammatory (Dekhane *et al.*, 2011), anti-tumor, anti-HCV (Rostom *et al.*, 2003), herbicidal (Zhou *et al.*, 2010) and insecticidal activities (Finkelstein & Strock, 1997). In view of such findings and as a continuation of our study on the synthesis of potential bio-active heterocyclic molecules, we report here the synthesis and crystal structure of the title compound.

In the title compound, the pyrazolidine ring is slightly twisted with an r.m.s. deviation from the mean plane of the 5 atoms forming the ring of 0.036 Å. The dihedral angle between this plane and that of the phenyl ring is 51.09 (4)° (Fig. 1).

S2. Experimental

To phosphorous oxychloride (0.1 mol, 10 ml), in a conical flask with a magnetic stirrer, dry dimethylformamide (35 ml) was added drop-wise with stirring at 303–308 K for 30 min. Then a solution of 1-phenylpyrazolidine-3,5-dione (0.05 mol, 8.8 g) in dimethylformamide (15 ml), was added drop-wise with continuous stirring while ensuring that the temperature did not exceed 318 K. The reaction mixture was stirred overnight and poured onto crushed ice. The solid product was collected by filtration and recrystallized from ethanol to give colourless crystals in 75% yield (m. p. 453–455 K).

S3. Refinement

H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached carbon atoms. The model was refined as a 2-component twin.
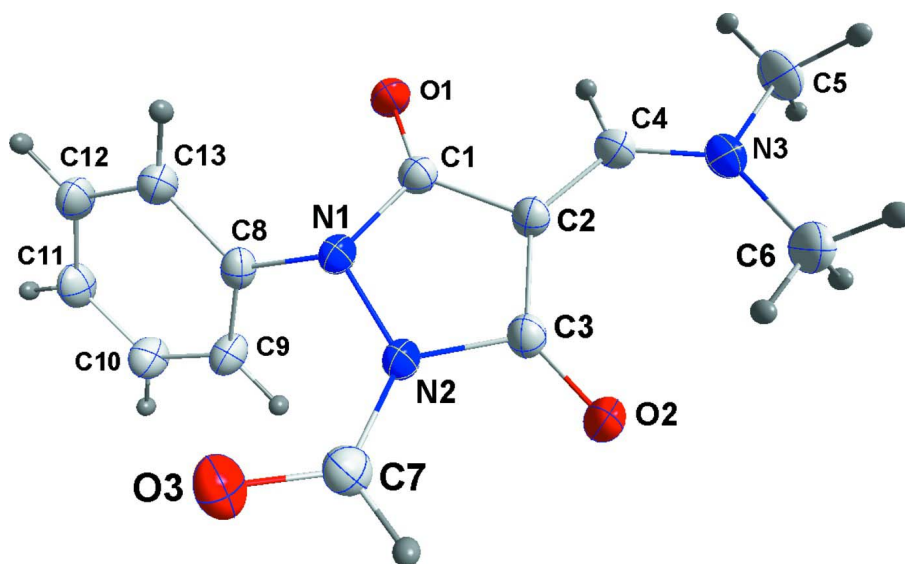
Figure 1

The title molecule with 50% probability ellipsoids.
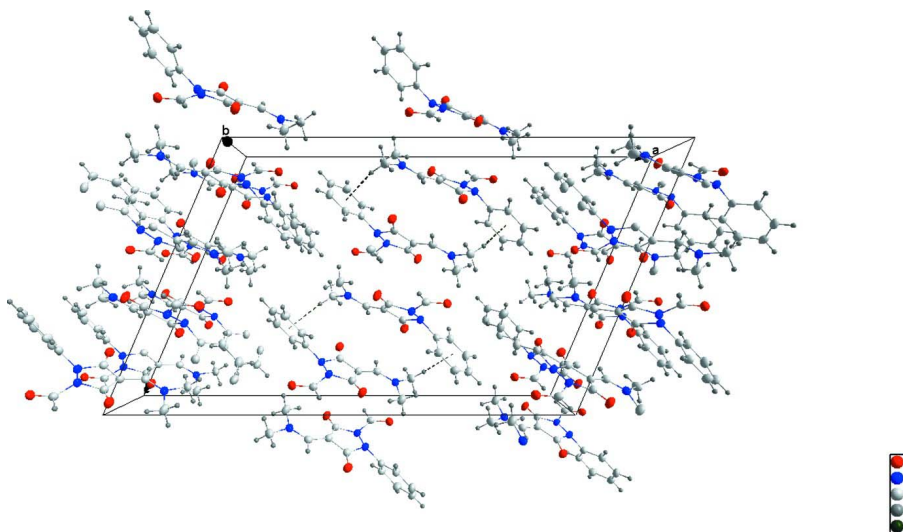
Figure 2

Packing viewed down the *b* axis. C—H···*π* interactions are shown by dotted lines.

(4*Z*)-4-[(Dimethylamino)methylidene]-3,5-dioxo-2-phenylpyrazolidine-1-carbaldehyde

Crystal data

$C_{13}H_{13}N_3O_3$	$F(000) = 1088$
$M_r = 259.26$	$D_x = 1.379$ Mg m^{-3}
Monoclinic, *C*2/*c*	Cu *Kα* radiation, $λ = 1.54178$ Å
$a = 26.4235\ (9)$ Å	Cell parameters from 9978 reflections
$b = 6.1033\ (2)$ Å	$θ = 3.6–72.3°$
$c = 16.8611\ (6)$ Å	$μ = 0.84$ mm^{-1}
$β = 113.272\ (1)°$	$T = 150$ K
$V = 2497.96\ (15)$ Å^3	Rod, colourless
$Z = 8$	$0.24 × 0.15 × 0.05$ mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer	$T_{min} = 0.82$, $T_{max} = 0.96$
Radiation source: INCOATEC IµS micro–focus source	26486 measured reflections
	4565 independent reflections
Mirror monochromator	3979 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.021$
ω scans	$\theta_{max} = 72.3°$, $\theta_{min} = 3.6°$
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)	$h = -32 \rightarrow 30$
	$k = -7 \rightarrow 7$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.104$	
$S = 1.04$	H-atom parameters constrained
4565 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.7347P]$
175 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.26$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Experimental. Analysis of 3764 reflections having I/σ(I) > 12 and chosen from
the full data set with *CELL_NOW* (Sheldrick, 2008) showed
the crystal to belong to the monoclinic system and to be twinned
by a 180° rotation about the *c** axis. The raw data were
processed using the multi-component version of *SAINT* under
control of the two-component orientation file generated by
CELL_NOW.

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. H-atoms were placed in
calculated positions (C—H = 0.95 - 0.98 Å) and included as riding
contributions with isotropic displacement parameters 1.2 - 1.5 times those
of the attached carbon atoms. The model was refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.43175 (4)	0.79022 (16)	0.28697 (7)	0.0296 (2)
O2	0.52891 (4)	0.15926 (16)	0.42906 (7)	0.0324 (3)
O3	0.37052 (4)	0.10698 (18)	0.39957 (6)	0.0316 (3)

N1	0.40831 (4)	0.46179 (18)	0.33205 (7)	0.0236 (3)
N2	0.43832 (4)	0.26978 (18)	0.36829 (7)	0.0239 (3)
N3	0.59876 (5)	0.64368 (19)	0.42207 (8)	0.0265 (3)
C1	0.44610 (5)	0.6170 (2)	0.32599 (8)	0.0233 (3)
C2	0.50109 (5)	0.5284 (2)	0.37179 (8)	0.0235 (3)
C3	0.49589 (5)	0.3060 (2)	0.39467 (8)	0.0242 (3)
C4	0.54556 (5)	0.6654 (2)	0.38045 (9)	0.0249 (3)
H4	0.5349	0.8001	0.3502	0.030*
C5	0.63539 (6)	0.8195 (3)	0.41755 (10)	0.0344 (3)
H5A	0.6133	0.9445	0.3861	0.052*
H5B	0.6580	0.7661	0.3874	0.052*
H5C	0.6594	0.8652	0.4761	0.052*
C6	0.62712 (6)	0.4598 (3)	0.47712 (10)	0.0344 (3)
H6A	0.6002	0.3471	0.4750	0.052*
H6B	0.6462	0.5109	0.5367	0.052*
H6C	0.6540	0.3978	0.4566	0.052*
C7	0.41757 (5)	0.1104 (2)	0.40511 (8)	0.0255 (3)
H7	0.4416	−0.0034	0.4367	0.031*
C8	0.35475 (5)	0.4373 (2)	0.26388 (8)	0.0235 (3)
C9	0.34078 (5)	0.2502 (2)	0.21315 (9)	0.0275 (3)
H9	0.3667	0.1349	0.2227	0.033*
C10	0.28831 (6)	0.2336 (3)	0.14813 (9)	0.0311 (3)
H10	0.2783	0.1062	0.1129	0.037*
C11	0.25040 (6)	0.4019 (3)	0.13433 (9)	0.0311 (3)
H11	0.2146	0.3899	0.0897	0.037*
C12	0.26490 (6)	0.5880 (2)	0.18593 (10)	0.0308 (3)
H12	0.2390	0.7031	0.1765	0.037*
C13	0.31717 (5)	0.6066 (2)	0.25127 (9)	0.0271 (3)
H13	0.3271	0.7333	0.2868	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0274 (5)	0.0239 (5)	0.0339 (5)	0.0033 (4)	0.0083 (4)	0.0053 (4)
O2	0.0221 (5)	0.0284 (5)	0.0409 (6)	0.0034 (4)	0.0063 (4)	0.0100 (4)
O3	0.0259 (5)	0.0404 (6)	0.0290 (5)	−0.0054 (4)	0.0115 (4)	0.0019 (4)
N1	0.0201 (5)	0.0227 (6)	0.0262 (6)	0.0027 (4)	0.0072 (4)	0.0031 (4)
N2	0.0190 (5)	0.0234 (6)	0.0267 (6)	0.0013 (4)	0.0062 (4)	0.0053 (4)
N3	0.0232 (5)	0.0306 (6)	0.0260 (6)	−0.0047 (4)	0.0099 (4)	−0.0026 (5)
C1	0.0241 (6)	0.0232 (6)	0.0227 (6)	0.0005 (5)	0.0093 (5)	−0.0009 (5)
C2	0.0211 (6)	0.0252 (7)	0.0233 (6)	0.0009 (5)	0.0077 (5)	0.0017 (5)
C3	0.0206 (6)	0.0268 (6)	0.0231 (6)	−0.0003 (5)	0.0063 (5)	0.0013 (5)
C4	0.0266 (6)	0.0250 (6)	0.0233 (6)	−0.0015 (5)	0.0102 (5)	−0.0005 (5)
C5	0.0296 (7)	0.0432 (8)	0.0314 (7)	−0.0132 (6)	0.0132 (6)	−0.0043 (7)
C6	0.0237 (6)	0.0348 (8)	0.0386 (8)	0.0007 (6)	0.0059 (6)	−0.0005 (6)
C7	0.0254 (6)	0.0271 (7)	0.0216 (6)	−0.0029 (5)	0.0066 (5)	0.0022 (5)
C8	0.0195 (6)	0.0289 (7)	0.0227 (6)	0.0010 (5)	0.0090 (5)	0.0033 (5)
C9	0.0247 (6)	0.0310 (7)	0.0258 (7)	0.0054 (5)	0.0089 (5)	0.0001 (5)

C10	0.0289 (7)	0.0344 (8)	0.0273 (7)	−0.0001 (6)	0.0082 (6)	−0.0029 (6)
C11	0.0212 (6)	0.0397 (8)	0.0281 (7)	0.0010 (6)	0.0053 (5)	0.0056 (6)
C12	0.0222 (6)	0.0319 (7)	0.0383 (8)	0.0060 (5)	0.0121 (6)	0.0072 (6)
C13	0.0240 (6)	0.0263 (7)	0.0326 (7)	0.0018 (5)	0.0128 (6)	0.0007 (5)

Geometric parameters (Å, º)

O1—C1	1.2234 (17)	C5—H5C	0.9800
O2—C3	1.2247 (17)	C6—H6A	0.9800
O3—C7	1.2096 (17)	C6—H6B	0.9800
N1—C1	1.4094 (17)	C6—H6C	0.9800
N1—N2	1.4116 (15)	C7—H7	0.9500
N1—C8	1.4356 (16)	C8—C9	1.387 (2)
N2—C7	1.3789 (17)	C8—C13	1.3898 (18)
N2—C3	1.4236 (16)	C9—C10	1.3903 (19)
N3—C4	1.3064 (17)	C9—H9	0.9500
N3—C6	1.4607 (19)	C10—C11	1.389 (2)
N3—C5	1.4669 (18)	C10—H10	0.9500
C1—C2	1.4538 (17)	C11—C12	1.389 (2)
C2—C4	1.4019 (18)	C11—H11	0.9500
C2—C3	1.4324 (19)	C12—C13	1.390 (2)
C4—H4	0.9500	C12—H12	0.9500
C5—H5A	0.9800	C13—H13	0.9500
C5—H5B	0.9800		
C1—N1—N2	107.25 (10)	N3—C6—H6A	109.5
C1—N1—C8	120.96 (11)	N3—C6—H6B	109.5
N2—N1—C8	117.89 (10)	H6A—C6—H6B	109.5
C7—N2—N1	121.70 (11)	N3—C6—H6C	109.5
C7—N2—C3	122.33 (11)	H6A—C6—H6C	109.5
N1—N2—C3	110.76 (10)	H6B—C6—H6C	109.5
C4—N3—C6	126.32 (12)	O3—C7—N2	123.82 (13)
C4—N3—C5	119.34 (12)	O3—C7—H7	118.1
C6—N3—C5	114.31 (12)	N2—C7—H7	118.1
O1—C1—N1	122.81 (12)	C9—C8—C13	121.19 (12)
O1—C1—C2	129.76 (12)	C9—C8—N1	121.16 (11)
N1—C1—C2	107.42 (11)	C13—C8—N1	117.64 (12)
C4—C2—C3	134.64 (12)	C8—C9—C10	119.07 (13)
C4—C2—C1	117.00 (12)	C8—C9—H9	120.5
C3—C2—C1	108.28 (11)	C10—C9—H9	120.5
O2—C3—N2	120.52 (12)	C11—C10—C9	120.43 (14)
O2—C3—C2	133.97 (12)	C11—C10—H10	119.8
N2—C3—C2	105.51 (11)	C9—C10—H10	119.8
N3—C4—C2	132.47 (13)	C10—C11—C12	119.85 (13)
N3—C4—H4	113.8	C10—C11—H11	120.1
C2—C4—H4	113.8	C12—C11—H11	120.1
N3—C5—H5A	109.5	C11—C12—C13	120.33 (13)
N3—C5—H5B	109.5	C11—C12—H12	119.8

H5A—C5—H5B	109.5	C13—C12—H12	119.8
N3—C5—H5C	109.5	C8—C13—C12	119.12 (13)
H5A—C5—H5C	109.5	C8—C13—H13	120.4
H5B—C5—H5C	109.5	C12—C13—H13	120.4
C1—N1—N2—C7	161.44 (12)	C1—C2—C3—N2	−4.26 (14)
C8—N1—N2—C7	−57.85 (16)	C6—N3—C4—C2	−2.8 (2)
C1—N1—N2—C3	6.44 (14)	C5—N3—C4—C2	179.28 (14)
C8—N1—N2—C3	147.14 (11)	C3—C2—C4—N3	−9.4 (3)
N2—N1—C1—O1	170.26 (12)	C1—C2—C4—N3	174.34 (14)
C8—N1—C1—O1	31.01 (19)	N1—N2—C7—O3	10.0 (2)
N2—N1—C1—C2	−8.87 (14)	C3—N2—C7—O3	162.12 (13)
C8—N1—C1—C2	−148.12 (11)	C1—N1—C8—C9	111.30 (15)
O1—C1—C2—C4	6.4 (2)	N2—N1—C8—C9	−23.84 (17)
N1—C1—C2—C4	−174.52 (11)	C1—N1—C8—C13	−69.53 (16)
O1—C1—C2—C3	−170.80 (13)	N2—N1—C8—C13	155.33 (12)
N1—C1—C2—C3	8.25 (14)	C13—C8—C9—C10	0.6 (2)
C7—N2—C3—O2	24.0 (2)	N1—C8—C9—C10	179.72 (13)
N1—N2—C3—O2	178.78 (12)	C8—C9—C10—C11	−0.2 (2)
C7—N2—C3—C2	−156.09 (12)	C9—C10—C11—C12	−0.2 (2)
N1—N2—C3—C2	−1.27 (14)	C10—C11—C12—C13	0.0 (2)
C4—C2—C3—O2	−0.8 (3)	C9—C8—C13—C12	−0.7 (2)
C1—C2—C3—O2	175.68 (15)	N1—C8—C13—C12	−179.87 (12)
C4—C2—C3—N2	179.21 (14)	C11—C12—C13—C8	0.4 (2)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1/C2/C3/N1/N2 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C6—H6*A*⋯O2	0.98	2.08	3.016 (2)	160
C5—H5*C*⋯O3[i]	0.98	2.52	3.1803 (19)	124
C7—H7⋯O2[ii]	0.95	2.29	3.0663 (16)	139
C5—H5*B*⋯Cg1[iii]	0.98	2.98	3.8823 (18)	153

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