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N-(3-Nitrophenyl)maleamic acid

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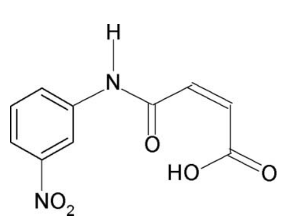
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.097; data-to-parameter ratio = 11.6.

In the title compound, $C_{10}H_8N_2O_5$, the molecule is slightly distorted from planarity. The molecular structure is stabilized by two intramolecular hydrogen bonds. The first is a short O—H···O hydrogen bond (H···O distance = 1.57 Å) within the maleamic acid unit and the second is a C—H···O hydrogen bond (H···O distance = 2.24 Å) which connects the amide group with the benzene ring. The nitro group is twisted by 6.2 (2)° out of the plane of the benzene ring. The crystal structure manifests a variety of hydrogen bonding. The packing is dominated by a strong intermolecular N—H···O interaction which links the molecules into chains running along the b axis. The chains within a plane are further assembled by three additional types of intermolecular C—H···O hydrogen bonds to form a sheet parallel to the ($\overline{1}01$) plane.

Related literature

For studies on the effect of ring- and side-chain substitutions on the crystal structures of amides, see: Gowda, Tokarčík, Kožíšek *et al.* (2010); Gowda *et al.* (2010*a*,*b*); Prasad *et al.* (2002). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{10}H_8N_2O_5$
M_r = 236.18
Monoclinic, $P2_1/c$
a = 7.9965 (2) Å
b = 14.0253 (3) Å
c = 9.1026 (2) Å
β = 100.147 (3)°
V = 1004.92 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 295 K
0.57 × 0.33 × 0.28 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.926, T_{max} = 0.971
17136 measured reflections
1793 independent reflections
1544 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.097
S = 1.08
1793 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O1	0.93	1.57	2.4978 (13)	176
C6—H6···O1	0.93	2.24	2.8302 (15)	121
N1—H1N···O3$^{\rm i}$	0.86	2.05	2.8929 (14)	167
C10—H10···O3$^{\rm i}$	0.93	2.51	3.2781 (17)	140
C3—H3···O5$^{\rm ii}$	0.93	2.57	3.2959 (17)	135
C9—H9···O4$^{\rm iii}$	0.93	2.51	3.1793 (17)	129
C8—H8···O2$^{\rm iii}$	0.93	2.57	3.4877 (17)	170

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z+1$; (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2039).

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supporting information

Acta Cryst. (2010). E**66**, o1671–o1672 [doi:10.1107/S1600536810022245]

N-(3-Nitrophenyl)maleamic acid

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S1. Comment

In the present study, as a part of studying the effect of ring and side chain substitutions on the crystal structures of biologically significant amides (Gowda *et al.*, 2010*a,b,c*; Prasad *et al.*, 2002), the crystal structure of *N*-(3-nitrophenyl)-maleamic acid (I) has been determined (Fig. 1). The conformation of the N—H in the amide segment is *anti* to the C=O bond and is also *anti* to the *meta*-nitro group in the phenyl ring.

In the maleamic acid moiety, the amide C=O bond is *anti* to the adjacent C—H bond, while the carboxyl C=O bond is *syn* to the adjacent C—H bond. The observed rare *anti* conformation of the C=O and O—H bonds of the acid group is similar to that obsrved in *N*-(2-methylphenyl)-maleamic acid (Gowda *et al.*, 2010*b*), *N*-(3-chlorophenyl)-maleamic acid (Gowda *et al.*, 2010*c*) and *N*-(3,5-dichlorophenyl)- maleamic acid (Gowda *et al.*, 2010*a*).

The molecule in (I) is slightly distorted from planarity as indicated by the dihedral angle of 4.5 (1)° between the least squares planes of the maleamic acid unit (r.m.s. deviation of 0.050 Å) and the phenyl ring. The molecular structure (Fig. 1) is stabilized by two intramolecular hydrogen bonds (Table 1). The first is a short O–H···O hydrogen bond ((H···O distance of 1.57 Å) within the maleamic acid unit; the second one is a C–H···O hydrogen bond (H···O distance of 2.24 Å) which connects the amide group with the phenyl ring. The nitro group - known to be a strong electron- withdrawing substituent - opens up the *ipso* C–C–C angle and narrows the two adjacent intracyclic angles. This fact is evident from the intracyclic bond angles C6–C7–C8, C5–C6–C7 and C7–C8–C9 of 123.99 (12)°, 117.49 (12)° and 117.64 (12)° respectively. The nitro group is twisted 6.2 (2)° out of the plane of the phenyl ring.

The crystal structure (Fig. 2) manifests a variety of hydrogen bonding. The packing is dominated by a strong intermolecular N–H···O interaction (H···O distance of 2.05 Å) which links the molecules into the chains running along the *b* axis. The chains within a plane are further assembled by additional three types of intermolecular C–H···O hydrogen bonds to form a sheet parallel to the (-1 0 1) plane (Bernstein *et al.*, 1995).

S2. Experimental

The solution of maleic anhydride (0.025 mol) in toluene (25 ml) was treated dropwise with the solution of 3-nitroaniline (0.025 mol) also in toluene (20 ml) with constant stirring. The resulting mixture was warmed with stirring for over 30 min and set aside for an additional 30 min at room temperature for completion of the reaction. The mixture was then treated with dilute hydrochloric acid to remove the unreacted 3-nitroaniline. The resultant solid *N*-(3-nitrophenyl)-maleamic acid was filtered under suction and washed thoroughly with water to remove the unreacted maleic anhydride and maleic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked by elemental analysis and characterized by its infrared spectra.

Prism like light brown single crystals used in X-ray diffraction studies were grown in an ethanol solution by slow evaporation at room temperature.

S3. Refinement

All H atoms were visible in difference maps. The positions of carboxyl and amide H atoms were tested in preliminary refinement using a soft restraints on the O–H and N–H distances. Finally, all H atoms were positioned with idealized geometry using a riding model with the distances C–H = 0.93 Å, N–H = 0.86 Å and O–H = 0.93 Å. The U_{iso}(H) values were set at 1.2U_{eq}(C aromatic, N) and 1.5U_{eq}(O).

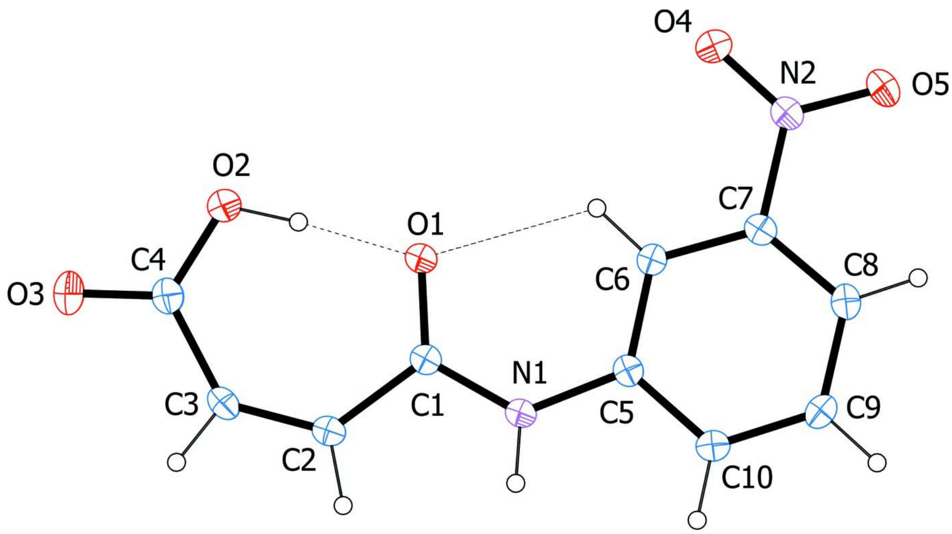

Figure 1

Molecular structure of (I) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Two short intramolecular bonds are indicated by dashed lines. H atoms are represented as small spheres of arbitrary radii.

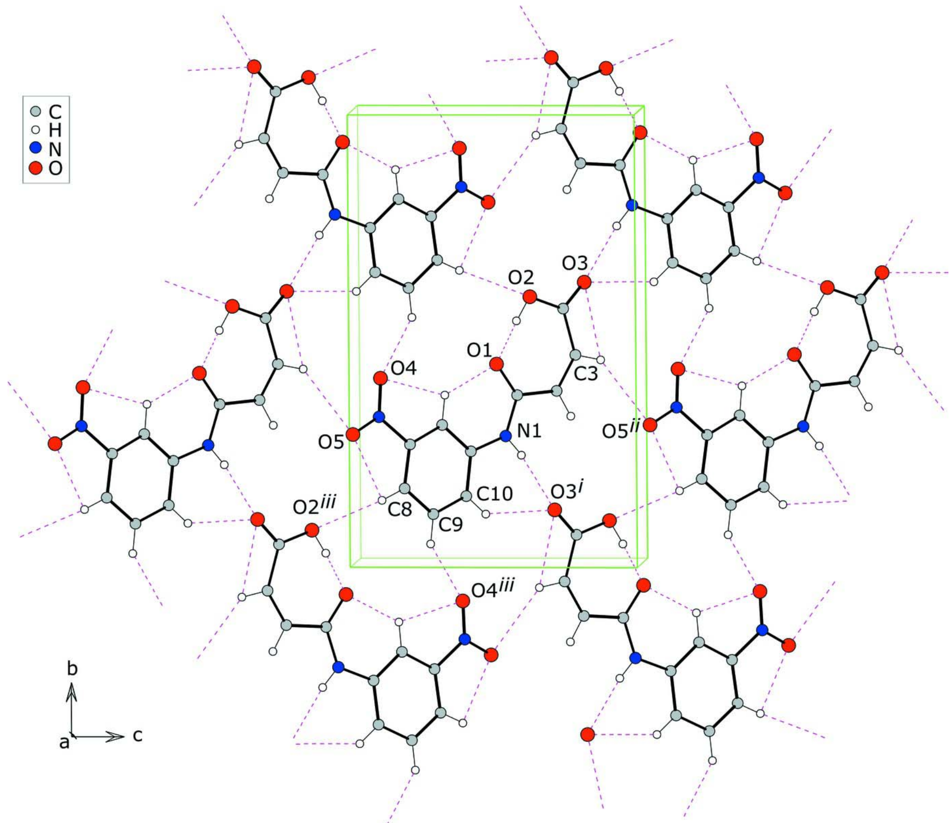

Figure 2

Part of crystal structure of (I) viewed down the *a* axis and showing a two-dimensional network of molecules linked by several types of intermolecular N–H···O and C–H···O hydrogen bonds (dashed lines). Symmetry codes (i): -*x* + 1, *y* - 1/2, -*z* + 3/2; (ii): *x* + 1, *y*, *z* + 1; (iii): -*x*, *y* - 1/2, -*z* + 1/2.

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Crystal data

$C_{10}H_8N_2O_5$
M_r = 236.18
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 7.9965 (2) Å
b = 14.0253 (3) Å
c = 9.1026 (2) Å
β = 100.147 (3)°
V = 1004.92 (4) Å^3
Z = 4
F(000) = 488
D_x = 1.561 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 10218 reflections
θ = 2.3–29.4°
μ = 0.13 mm^{-1}
T = 295 K
Prism, light brown
0.57 × 0.33 × 0.28 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Graphite monochromator
Detector resolution: 10.434 pixels mm^{-1}
ω scans
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.926, T_{max} = 0.971
17136 measured reflections
1793 independent reflections
1544 reflections with $I > 2\sigma(I)$

R_{int} = 0.023
θ_{max} = 25.1°, θ_{min} = 2.6°
h = −9→9
k = −16→16
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.097
S = 1.08
1793 reflections
154 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.1002P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 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}
C1	0.30465 (16)	0.37499 (8)	0.57539 (15)	0.0361 (3)
C2	0.44044 (17)	0.38197 (9)	0.70806 (15)	0.0406 (3)
H2	0.4755	0.3245	0.7543	0.049*
C3	0.51952 (16)	0.45956 (10)	0.77048 (15)	0.0418 (3)
H3	0.5991	0.4471	0.8559	0.05*
C4	0.50454 (17)	0.56183 (10)	0.72945 (15)	0.0421 (3)
C5	0.13141 (15)	0.25342 (9)	0.41799 (14)	0.0342 (3)
C6	0.02666 (15)	0.31456 (9)	0.32224 (14)	0.0365 (3)
H6	0.0378	0.3804	0.3312	0.044*
C7	−0.09413 (16)	0.27380 (9)	0.21369 (13)	0.0357 (3)
C8	−0.11652 (17)	0.17731 (9)	0.19464 (16)	0.0422 (3)
H8	−0.1995	0.1528	0.1196	0.051*
C9	−0.01165 (19)	0.11799 (9)	0.29057 (17)	0.0476 (4)
H9	−0.0236	0.0522	0.2806	0.057*
C10	0.11119 (17)	0.15542 (9)	0.40145 (15)	0.0417 (3)
H10	0.181	0.1146	0.4656	0.05*
N1	0.25906 (14)	0.28534 (7)	0.53544 (12)	0.0389 (3)
H1N	0.3151	0.2413	0.5885	0.047*
N2	−0.20553 (14)	0.33698 (8)	0.11149 (12)	0.0442 (3)
O1	0.23643 (13)	0.44532 (6)	0.50694 (11)	0.0487 (3)
O2	0.38964 (13)	0.59058 (7)	0.61814 (12)	0.0547 (3)
H2A	0.3292	0.5383	0.5739	0.082*

O3	0.60038 (15)	0.61868 (8)	0.80038 (13)	0.0649 (3)
O4	−0.17942 (14)	0.42253 (7)	0.11665 (12)	0.0596 (3)
O5	−0.32118 (15)	0.30062 (8)	0.02350 (14)	0.0752 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0377 (7)	0.0306 (7)	0.0363 (7)	0.0005 (5)	−0.0039 (6)	0.0012 (5)
C2	0.0439 (7)	0.0332 (7)	0.0393 (7)	0.0036 (5)	−0.0078 (6)	0.0031 (5)
C3	0.0418 (7)	0.0415 (8)	0.0355 (7)	0.0014 (5)	−0.0115 (6)	−0.0003 (6)
C4	0.0467 (8)	0.0376 (7)	0.0381 (7)	−0.0022 (6)	−0.0034 (6)	−0.0044 (6)
C5	0.0359 (7)	0.0313 (7)	0.0326 (7)	−0.0003 (5)	−0.0018 (5)	−0.0013 (5)
C6	0.0406 (7)	0.0278 (6)	0.0373 (7)	−0.0016 (5)	−0.0035 (6)	−0.0011 (5)
C7	0.0372 (7)	0.0336 (7)	0.0334 (7)	0.0013 (5)	−0.0014 (5)	0.0014 (5)
C8	0.0431 (7)	0.0354 (7)	0.0429 (7)	−0.0039 (5)	−0.0069 (6)	−0.0052 (5)
C9	0.0559 (9)	0.0260 (7)	0.0547 (9)	−0.0017 (6)	−0.0071 (7)	−0.0031 (6)
C10	0.0452 (7)	0.0310 (7)	0.0441 (7)	0.0027 (5)	−0.0050 (6)	0.0023 (6)
N1	0.0424 (6)	0.0290 (5)	0.0388 (6)	0.0021 (4)	−0.0106 (5)	0.0024 (4)
N2	0.0475 (7)	0.0373 (7)	0.0413 (6)	0.0004 (5)	−0.0100 (5)	0.0006 (5)
O1	0.0556 (6)	0.0307 (5)	0.0493 (6)	0.0003 (4)	−0.0201 (5)	0.0031 (4)
O2	0.0659 (7)	0.0326 (6)	0.0549 (6)	−0.0029 (4)	−0.0190 (5)	0.0035 (4)
O3	0.0759 (8)	0.0444 (6)	0.0630 (7)	−0.0147 (5)	−0.0195 (6)	−0.0104 (5)
O4	0.0713 (7)	0.0326 (6)	0.0637 (7)	−0.0011 (5)	−0.0194 (5)	0.0051 (5)
O5	0.0769 (8)	0.0490 (7)	0.0778 (8)	−0.0031 (6)	−0.0463 (7)	0.0003 (6)

Geometric parameters (Å, º)

C1—O1	1.2406 (15)	C6—H6	0.93
C1—N1	1.3414 (16)	C7—C8	1.3721 (18)
C1—C2	1.4782 (19)	C7—N2	1.4670 (16)
C2—C3	1.3343 (19)	C8—C9	1.378 (2)
C2—H2	0.93	C8—H8	0.93
C3—C4	1.4817 (19)	C9—C10	1.3820 (19)
C3—H3	0.93	C9—H9	0.93
C4—O3	1.2106 (17)	C10—H10	0.93
C4—O2	1.3059 (17)	N1—H1N	0.86
C5—C10	1.3890 (18)	N2—O4	1.2174 (15)
C5—C6	1.3925 (17)	N2—O5	1.2231 (15)
C5—N1	1.4145 (16)	O2—H2A	0.93
C6—C7	1.3784 (17)		
O1—C1—N1	122.32 (12)	C8—C7—N2	117.68 (11)
O1—C1—C2	123.53 (11)	C6—C7—N2	118.33 (11)
N1—C1—C2	114.14 (10)	C7—C8—C9	117.64 (12)
C3—C2—C1	128.80 (12)	C7—C8—H8	121.2
C3—C2—H2	115.6	C9—C8—H8	121.2
C1—C2—H2	115.6	C8—C9—C10	120.55 (12)
C2—C3—C4	132.14 (13)	C8—C9—H9	119.7

C2—C3—H3	113.9	C10—C9—H9	119.7
C4—C3—H3	113.9	C9—C10—C5	120.61 (12)
O3—C4—O2	120.21 (13)	C9—C10—H10	119.7
O3—C4—C3	119.18 (13)	C5—C10—H10	119.7
O2—C4—C3	120.60 (12)	C1—N1—C5	128.83 (11)
C10—C5—C6	119.72 (12)	C1—N1—H1N	115.6
C10—C5—N1	116.73 (11)	C5—N1—H1N	115.6
C6—C5—N1	123.54 (11)	O4—N2—O5	122.75 (11)
C7—C6—C5	117.49 (12)	O4—N2—C7	119.35 (10)
C7—C6—H6	121.3	O5—N2—C7	117.90 (11)
C5—C6—H6	121.3	C4—O2—H2A	109.5
C8—C7—C6	123.99 (12)		

O1—C1—C2—C3	−4.7 (2)	C8—C9—C10—C5	−0.1 (2)
N1—C1—C2—C3	176.01 (13)	C6—C5—C10—C9	0.2 (2)
C1—C2—C3—C4	−1.9 (3)	N1—C5—C10—C9	179.35 (12)
C2—C3—C4—O3	−175.18 (15)	O1—C1—N1—C5	−1.3 (2)
C2—C3—C4—O2	4.8 (2)	C2—C1—N1—C5	177.97 (11)
C10—C5—C6—C7	−0.04 (18)	C10—C5—N1—C1	179.91 (12)
N1—C5—C6—C7	−179.15 (11)	C6—C5—N1—C1	−1.0 (2)
C5—C6—C7—C8	−0.15 (19)	C8—C7—N2—O4	−173.53 (12)
C5—C6—C7—N2	−179.87 (11)	C6—C7—N2—O4	6.21 (18)
C6—C7—C8—C9	0.2 (2)	C8—C7—N2—O5	6.09 (18)
N2—C7—C8—C9	179.91 (12)	C6—C7—N2—O5	−174.17 (12)
C7—C8—C9—C10	0.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O1	0.93	1.57	2.4978 (13)	176
C6—H6···O1	0.93	2.24	2.8302 (15)	121
N1—H1*N*···O3^{i}	0.86	2.05	2.8929 (14)	167
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Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) *x*+1, *y*, *z*+1; (iii) −*x*, *y*−1/2, −*z*+1/2.