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Crystal structure of (*E*,*E*)-2′,4′-dihydroxyacetophenone azine dimethylformamide disolvate

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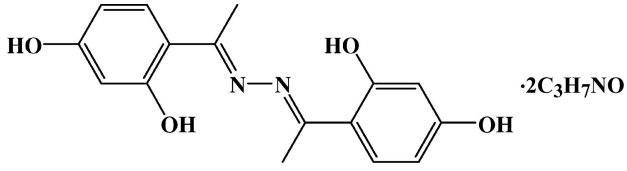
In the title compound {systematic name: 4,4′-[1,1′-(hydrazinediylidene)bis(ethan-1-yl-1-ylidene)]bis(benzene-1,3-diol)}, $C_{16}H_{16}N_2O_4\cdot 2C_3H_7NO$, the (*E*,*E*)-2′,4′-dihydroxyacetophenone azine molecule is centrosymmetric, the mid-point of the N—N bond being located on an inversion centre. All the non-H atoms of the azine molecule are approximately coplanar, the maximum deviation being 0.017 (2) Å. An intramolecular O—H···N hydrogen bond occurs between the azine N atom and the hydroxy group. In the crystal, azine and dimethylformamide solvent molecules are linked by O—H···O hydrogen bonds.

1. Chemical context

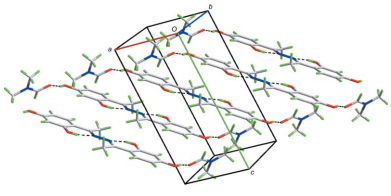
Hydrazones are important compounds due to their possible applications in material and coordination chemistry. Fluorescence properties of hydrazones have been reported (Qin *et al.*, 2009). Many organometallic compounds containing acylhydrazone ligands have also been synthesized for their potential magneto-chemical properties (Guo *et al.*, 2010). In particular, they have received increasing interest for their biological activity as antioxidants (Kitaev *et al.*, 1970), and their antimicrobial (Ramamohan *et al.*, 1995) and antiviral properties (El-Tabl *et al.*, 2008; Rollas & Küçükgüzel, 2007).



Although 2′,4′-dihydroxyacetophenone azine has been prepared and studied as a fluorescent probe, its structure has not been reported. As a part of our studies on synthesis and structural peculiarities of Schiff base ligands derived from 2′,4′-dihydroxyacetophenone and hydrazine, we determined the structure of the title compound, (*E*,*E*)-2′,4′-dihydroxyacetophenone azine dimethylformamide disolvate, (I).

2. Structural commentary

The molecular structure of the title compound is depicted in Fig. 1. The asymmetric unit contains one half-molecule of (*E*,*E*)-2′,4′-dihydroxyacetophenone azine and one dimethylformamide (DMF) molecule. The complete azine molecule is centrosymmetric and exists in an *E*,*E* configuration with respect to the two C=N bonds. The N1—C2 bond length of 1.301 (3) Å shows double-bond character. The C—O bond lengths [1.349 (3) and 1.358 (3) Å] are comparable with



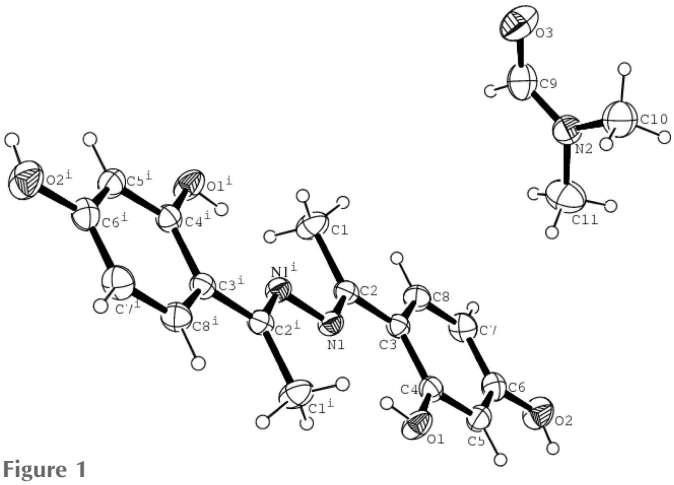


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one DMF solvent molecule is shown. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

similar bonds in related structures (Chantrapromma *et al.*, 2011; Tai *et al.*, 2008). All the non-H atoms of the azine molecule are approximately coplanar. The nine atoms (*i.e.* N1, C1 and C2, and the six C atoms in the benzene ring) are essentially planar, with a mean deviation of 0.0024 Å. Each hydroxy group is nearly coplanar with its attached benzene ring; the r.m.s. deviation is 0.0045 Å for the seven non-H atoms. Intramolecular O—H···N hydrogen bonds exist in the azine molecule (Table 1).

3. Supramolecular features

In the crystal of (I), intermolecular O—H···O hydrogen bonds exist between azine molecules and DMF molecules (Table 1 and Fig. 2).

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.82	2.543 (2)	147
O2—H2···O3^{i}	0.82	1.84	2.649 (3)	171

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

4. Database survey

A search of Cambridge Structural Database (Groom & Allen, 2014) for acetophenone azine gave 105 hits (excluding organometallics). There are four reported crystal structures of acetophenone azine containing hydroxy groups at the 2-position of benzene rings: (*E*,*E*)-2,2′-(1,1′-azinodiethylidyne)-diphenol (Tai *et al.*, 2008), (*E*,*E*)-4,4′-dichloro-2,2′-(1,1′-azinodiethylidyne)diphenol (Chang *et al.*, 2007), (*E*,*E*)-3,3′-diethoxy-2,2′-(1,1′-azinodiethylidyne)diphenol (Fayos *et al.*, 1980) and (*E*,*E*)-4,4′-dimethoxy-2,2′-(1,1′-azinodiethylidyne)-diphenol (Zhang *et al.*, 2008).

5. Synthesis and crystallization

A mixture of 2′,4′-dihydroxyacetophenone (3.06 g, 20 mmol), hydrazine sulfate (1.28 g, 10 mmol) and triethylamine (3.03 g, 30 mmol) in ethanol (40 ml) was heated under reflux for 24 h. After cooling, the precipitate was filtrated and washed with water to afford a yellow solid. Crystals of the title compound suitable for X-ray diffraction were obtained by slow evaporation of a solution of the solid in DMF at room temperature for 5 d (yield 1.20 g, 75%; m.p: 484–485 K). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.59 (*s*, 2H, OH), 10.14 (*s*, 2H, OH), 7.58–7.61 (*d*, 2H, ArH), 6.37–6.41 (*d*, 2H, ArH), 6.30–6.31 (*s*, 2H, ArH), 3.34 (*d*, 6H, CH_3).

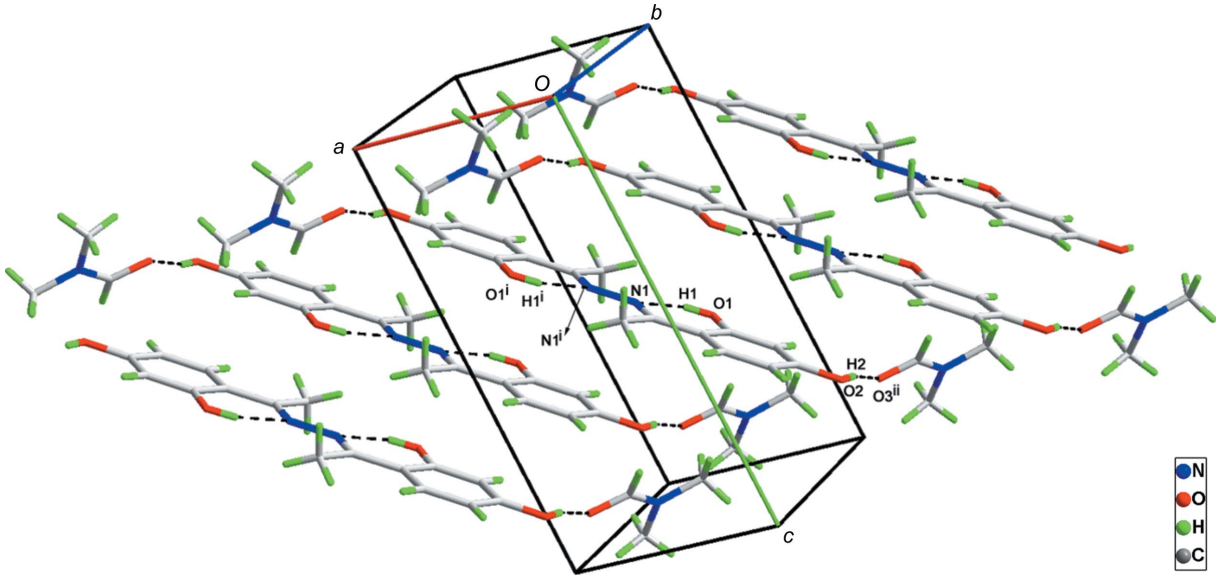


Figure 2
The crystal packing of the title compound. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y+1, z$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{16}N_2O_4{\cdot}2C_3H_7NO$
M_r	446.50
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	298
a, b, c (Å)	6.1616 (7), 7.3109 (8), 13.4537 (15)
α, β, γ (°)	96.771 (1), 103.049 (2), 96.607 (1)
V (Å^3)	579.96 (11)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.48 × 0.43 × 0.21
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.956, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2902, 2001, 1313
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.187, 1.02
No. of reflections	2001
No. of parameters	149
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.25

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed geometrically (C—H = 0.93–0.96 Å and O—H = 0.82 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms or 1.5U_{eq}(C,O) for methyl and hydroxy groups.

Acknowledgements

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supporting information

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Crystal structure of (*E*,*E*)-2′,4′-dihydroxyacetophenone azine dimethylformamide disolvate

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Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); 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* (Sheldrick, 2008).

4,4′-[1,1′-(Hydrazinediylidene)bis(ethan-1-yl-1-ylidene)]bis(benzene-1,3-diol)

Crystal data

$C_{16}H_{16}N_2O_4 \cdot 2C_3H_7NO$
$M_r = 446.50$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.1616$ (7) Å
$b = 7.3109$ (8) Å
$c = 13.4537$ (15) Å
$\alpha = 96.771$ (1)°
$\beta = 103.049$ (2)°
$\gamma = 96.607$ (1)°
$V = 579.96$ (11) Å^3
$Z = 1$
$F(000) = 238$
$D_x = 1.278$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1119 reflections
$\theta = 3.0$–26.5°
$\mu = 0.09$ mm^{-1}
$T = 298$ K
Block, colorless
0.48 × 0.43 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.956$, $T_{max} = 0.981$
2902 measured reflections
2001 independent reflections
1313 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.0°$
$h = -6 \rightarrow 7$
$k = -8 \rightarrow 7$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.187$
$S = 1.02$
2001 reflections
149 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

$w = 1/[\sigma^2(F_o^2) + (0.1079P)^2 + 0.0859P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.17 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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}
N1	0.4279 (3)	0.5237 (2)	0.53085 (13)	0.0391 (5)
N2	0.5727 (4)	0.1587 (3)	0.91556 (16)	0.0566 (6)
O1	0.2575 (3)	0.7659 (2)	0.62846 (12)	0.0537 (5)
H1	0.3372	0.7270	0.5919	0.081*
O2	−0.2843 (3)	0.5582 (3)	0.80524 (14)	0.0679 (6)
H2	−0.2793	0.6712	0.8190	0.102*
O3	0.7469 (4)	−0.0813 (3)	0.87057 (18)	0.0899 (8)
C1	0.3219 (5)	0.1857 (3)	0.5203 (2)	0.0574 (7)
H1A	0.2229	0.1462	0.4531	0.086*
H1B	0.2779	0.1098	0.5681	0.086*
H1C	0.4737	0.1732	0.5172	0.086*
C2	0.3080 (3)	0.3858 (3)	0.55569 (15)	0.0374 (6)
C3	0.1542 (3)	0.4334 (3)	0.62014 (15)	0.0368 (6)
C4	0.1368 (4)	0.6208 (3)	0.65420 (16)	0.0403 (6)
C5	−0.0090 (4)	0.6624 (3)	0.71594 (16)	0.0458 (6)
H5	−0.0180	0.7861	0.7380	0.055*
C6	−0.1404 (4)	0.5221 (4)	0.74482 (17)	0.0479 (6)
C7	−0.1270 (4)	0.3382 (4)	0.71238 (18)	0.0528 (7)
H7	−0.2153	0.2431	0.7316	0.063*
C8	0.0176 (4)	0.2968 (3)	0.65154 (17)	0.0472 (6)
H8	0.0249	0.1723	0.6304	0.057*
C9	0.5795 (5)	−0.0016 (5)	0.8617 (2)	0.0696 (9)
H9	0.4489	−0.0589	0.8136	0.084*
C10	0.7669 (5)	0.2551 (5)	0.9909 (2)	0.0808 (9)
H10A	0.8729	0.1706	1.0084	0.121*
H10B	0.7228	0.3039	1.0516	0.121*
H10C	0.8355	0.3556	0.9632	0.121*
C11	0.3699 (5)	0.2460 (5)	0.8988 (3)	0.0889 (10)
H11A	0.2480	0.1611	0.8530	0.133*
H11B	0.3951	0.3568	0.8687	0.133*
H11C	0.3324	0.2778	0.9635	0.133*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0427 (11)	0.0333 (11)	0.0416 (10)	0.0063 (8)	0.0117 (8)	0.0035 (8)
N2	0.0545 (13)	0.0620 (15)	0.0553 (12)	0.0128 (11)	0.0150 (10)	0.0088 (11)
O1	0.0704 (11)	0.0331 (10)	0.0647 (11)	0.0015 (8)	0.0367 (9)	0.0024 (7)
O2	0.0738 (13)	0.0718 (14)	0.0713 (12)	0.0124 (10)	0.0428 (10)	0.0122 (10)
O3	0.0897 (16)	0.0827 (17)	0.1017 (17)	0.0266 (14)	0.0354 (13)	−0.0059 (13)
C1	0.0708 (17)	0.0345 (14)	0.0745 (17)	0.0076 (12)	0.0332 (14)	0.0080 (12)
C2	0.0380 (12)	0.0337 (12)	0.0377 (11)	0.0037 (9)	0.0037 (9)	0.0065 (9)
C3	0.0383 (12)	0.0346 (12)	0.0351 (11)	0.0028 (9)	0.0048 (9)	0.0057 (9)
C4	0.0450 (13)	0.0378 (13)	0.0364 (11)	0.0024 (10)	0.0078 (10)	0.0064 (9)
C5	0.0532 (14)	0.0414 (14)	0.0427 (12)	0.0066 (11)	0.0136 (11)	0.0020 (10)
C6	0.0451 (13)	0.0583 (16)	0.0411 (12)	0.0065 (11)	0.0120 (10)	0.0081 (11)
C7	0.0548 (15)	0.0502 (16)	0.0561 (15)	−0.0022 (12)	0.0199 (12)	0.0155 (11)
C8	0.0539 (14)	0.0385 (14)	0.0497 (13)	0.0031 (11)	0.0137 (11)	0.0102 (10)
C9	0.0675 (19)	0.081 (2)	0.0575 (16)	−0.0021 (16)	0.0183 (14)	0.0061 (15)
C10	0.078 (2)	0.075 (2)	0.078 (2)	0.0069 (17)	0.0043 (17)	0.0000 (16)
C11	0.069 (2)	0.102 (3)	0.102 (2)	0.0268 (19)	0.0191 (18)	0.032 (2)

Geometric parameters (Å, º)

N1—C2	1.301 (3)	C3—C4	1.417 (3)
N1—N1^{i}	1.391 (3)	C4—C5	1.389 (3)
N2—C9	1.313 (4)	C5—C6	1.380 (3)
N2—C10	1.430 (4)	C5—H5	0.9300
N2—C11	1.453 (3)	C6—C7	1.381 (3)
O1—C4	1.349 (3)	C7—C8	1.374 (3)
O1—H1	0.8200	C7—H7	0.9300
O2—C6	1.358 (3)	C8—H8	0.9300
O2—H2	0.8200	C9—H9	0.9300
O3—C9	1.232 (3)	C10—H10A	0.9600
C1—C2	1.503 (3)	C10—H10B	0.9600
C1—H1A	0.9600	C10—H10C	0.9600
C1—H1B	0.9600	C11—H11A	0.9600
C1—H1C	0.9600	C11—H11B	0.9600
C2—C3	1.465 (3)	C11—H11C	0.9600
C3—C8	1.396 (3)		
C2—N1—N1^{i}	116.3 (2)	O2—C6—C5	122.1 (2)
C9—N2—C10	120.9 (2)	O2—C6—C7	118.0 (2)
C9—N2—C11	121.2 (3)	C5—C6—C7	119.9 (2)
C10—N2—C11	117.9 (3)	C8—C7—C6	119.6 (2)
C4—O1—H1	109.5	C8—C7—H7	120.2
C6—O2—H2	109.5	C6—C7—H7	120.2
C2—C1—H1A	109.5	C7—C8—C3	122.9 (2)
C2—C1—H1B	109.5	C7—C8—H8	118.6
H1A—C1—H1B	109.5	C3—C8—H8	118.6

C2—C1—H1C	109.5	O3—C9—N2	124.5 (3)
H1A—C1—H1C	109.5	O3—C9—H9	117.8
H1B—C1—H1C	109.5	N2—C9—H9	117.8
N1—C2—C3	116.96 (19)	N2—C10—H10A	109.5
N1—C2—C1	122.62 (19)	N2—C10—H10B	109.5
C3—C2—C1	120.4 (2)	H10A—C10—H10B	109.5
C8—C3—C4	116.5 (2)	N2—C10—H10C	109.5
C8—C3—C2	121.9 (2)	H10A—C10—H10C	109.5
C4—C3—C2	121.6 (2)	H10B—C10—H10C	109.5
O1—C4—C5	117.0 (2)	N2—C11—H11A	109.5
O1—C4—C3	122.42 (19)	N2—C11—H11B	109.5
C5—C4—C3	120.6 (2)	H11A—C11—H11B	109.5
C6—C5—C4	120.7 (2)	N2—C11—H11C	109.5
C6—C5—H5	119.7	H11A—C11—H11C	109.5
C4—C5—H5	119.7	H11B—C11—H11C	109.5

N1^{i}—N1—C2—C3	−179.63 (19)	C3—C4—C5—C6	−0.3 (3)
N1^{i}—N1—C2—C1	−0.1 (3)	C4—C5—C6—O2	179.9 (2)
N1—C2—C3—C8	−179.94 (18)	C4—C5—C6—C7	0.2 (3)
C1—C2—C3—C8	0.5 (3)	O2—C6—C7—C8	−179.7 (2)
N1—C2—C3—C4	−0.2 (3)	C5—C6—C7—C8	0.0 (4)
C1—C2—C3—C4	−179.69 (19)	C6—C7—C8—C3	−0.1 (4)
C8—C3—C4—O1	−179.28 (19)	C4—C3—C8—C7	−0.1 (3)
C2—C3—C4—O1	0.9 (3)	C2—C3—C8—C7	179.7 (2)
C8—C3—C4—C5	0.3 (3)	C10—N2—C9—O3	0.1 (4)
C2—C3—C4—C5	−179.47 (19)	C11—N2—C9—O3	178.5 (3)
O1—C4—C5—C6	179.3 (2)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.82	2.543 (2)	147
O2—H2···O3^{ii}	0.82	1.84	2.649 (3)	171

Symmetry code: (ii) *x*−1, *y*+1, *z*.