organic compounds

2-Methyl-4-phenyl-3,4-dihydro-quinazoline

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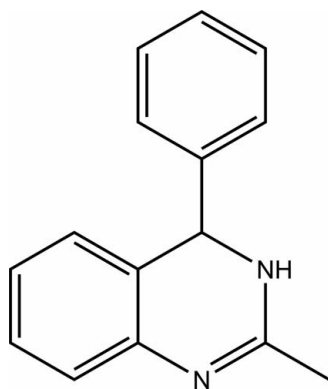Correspondence e-mail: arto.m.valkonen@jyu.fi

The title compound, $C_{15}H_{14}N_2$, was formed during the lithiation of 2-methylquinazoline with phenyllithium followed by hydrolysis of the intermediate lithium 2-methyl-4-phenyl-4H-quinazolin-3-ide. NMR spectra as well as single-crystal X-ray structural data indicate that the reaction product to have the same structure in chloroform solution as in the crystalline state. The phenyl substituent is twisted out of the plane of the 3,4-dihydroquinazoline ring system by 86.47 (7)°. In the crystal, intermolecular N—H⋯N interactions connect the molecules into infinite chains.

Related literature

For organolithium compounds and lithiation, see: Gawinecki *et al.* (2006); Kolehmainen *et al.* (2000); Wakefield (1976); Armarego (1967). For previous characterizations of the title compound, see: Suri *et al.* (1993). For related structures, see: Rajnikant *et al.* (2002).

Experimental

Crystal data

$C_{15}H_{14}N_2$	$Z = 3$
$M_r = 222.28$	Mo $K\alpha$ radiation
Trigonal, $P3_1$	$\mu = 0.07$ mm^{-1}
$a = 9.5600$ (4) Å	$T = 123$ K
$c = 11.2569$ (5) Å	$0.35 \times 0.13 \times 0.12$ mm
$V = 890.97$ (7) Å^3	

Data collection

Bruker–Nonius KappaCCD with APEXII detector diffractometer	1468 independent reflections
6729 measured reflections	1215 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	1 restraint
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
1468 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
155 parameters	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3⋯N1[i]	0.88	2.04	2.908 (3)	169

Symmetry code: (i) $-y, x-y+1, z+\frac{1}{3}$.

Data collection: *COLLECT* (Bruker, 2008); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae, *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2274).

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supporting information

2-Methyl-4-phenyl-3,4-dihydroquinazoline

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S1. Comment

Addition of phenyllithium to 2-methylquinazoline takes place exclusively at the 3,4-position (neither 2-methyl-2-phenyl-1,2-dihydroquinazoline nor 2-methyl-4-phenyl-1,4-dihydroquinazoline were detected in the reaction mixture). Susceptibility of quinazolines to undergo the nucleophilic addition to their 3,4-double bonds has been reported earlier (Suri *et al.*, 1993). It is also known that 4-substituted 3,4-dihydroquinazolines can be generated from quinazolines when treated with organometallic compounds (Armarego, 1967). Furthermore, low susceptibility of 2-methyl group to lithiation precludes 2-methylquinazoline to be used as a starting material in syntheses of the important C_{exo}-substituted 2-methylquinazolines (Wakefield, 1976; Kolehmainen *et al.*, 2000; Gawinecki *et al.*, 2006).

In crystalline state the title compound shows the 3,4-dihydroquinazoline moiety to be planar (Fig. 1). The phenyl substituent is twisted out of plane of the moiety by 86.47 (7) °, which is rather close to the twist (79.3 (1) °) found in 2-methyl-4-phenyl-3,4-dihydroquinazolinium chloride (Rajnikant *et al.*, 2002). Intermolecular N3—H···N1 hydrogen bonds (-*y*, *x*-*y* + 1, *z* + 1/3 direction) define the supramolecular structure and connect the molecules to infinite helical chains (Fig. 2). Unfortunately, no reliable determination of the absolute structure (or handedness of helix) is possible by X-ray crystallography.

S2. Experimental

A solution of 2-methyl-quinazoline (10.09 g, 0.07 mol) in absolute ethyl ether (100 ml) was added dropwise with stirring to a solution of phenyllithium [obtained by a standard method starting from freshly distilled bromobenzene (15.70 g, 0.1 mol), absolute ethyl ether (0.5 *L*) and lithium (2.80 g, 0.4 mol)]. The reaction mixture was stirred at room temperature for additional 2 h and the reaction was quenched by addition of water (0.5 *L*). The organic layer was combined with the ether extracts of the water layer, dried (K_2CO_3) and evaporated to dryness. The crude solid product was recrystallized from ethanol to give white crystals (51%) melting at 168–170 °C [lit. mp 168–170 °C (Suri *et al.*, 1993)]. ^{1}H NMR (CDCl$_3$): δ (p.p.m.) = 7.26–7.34 (m, 5H, H12—H16), 7.13 (dd, 1H, H7), 7.02 (d, 1H, H8), 6.90 (dd, 1H, H6), 6.71 (d, 1H, H5), 5.67 (s, 1H, H4), 2.02 (s, 3H, CH3). ^{13}C NMR (CDCl$_3$): δ (p.p.m.) = 153.9 (C2), 145.3 (C11), 140.6 (C9), 128.1 (C7), 127.8 (C14), 128.7 (C13, C15), 127.3 (C12, C16), 126.7 (C5), 124.1 (C6), 123.3 (C10), 58.1 (C4), 22.5 (C17).

Suitable single crystals for X-ray diffraction were obtained by very slow evaporation of analytical sample from NMR-tube, where CDCl$_3$ was used as a solvent.

S3. Refinement

In the absence of significant anomalous disperson effects, Friedel pairs were averaged. All H atoms were visible in electron density maps, but were calculated at their idealized positions and allowed to ride on their parent atoms at C—H distances of 0.95 Å (aromatic), 0.98 Å (methyl), 1.00 Å (methine), and N—H distance of 0.88 Å, with U_{iso}(H) of 1.2

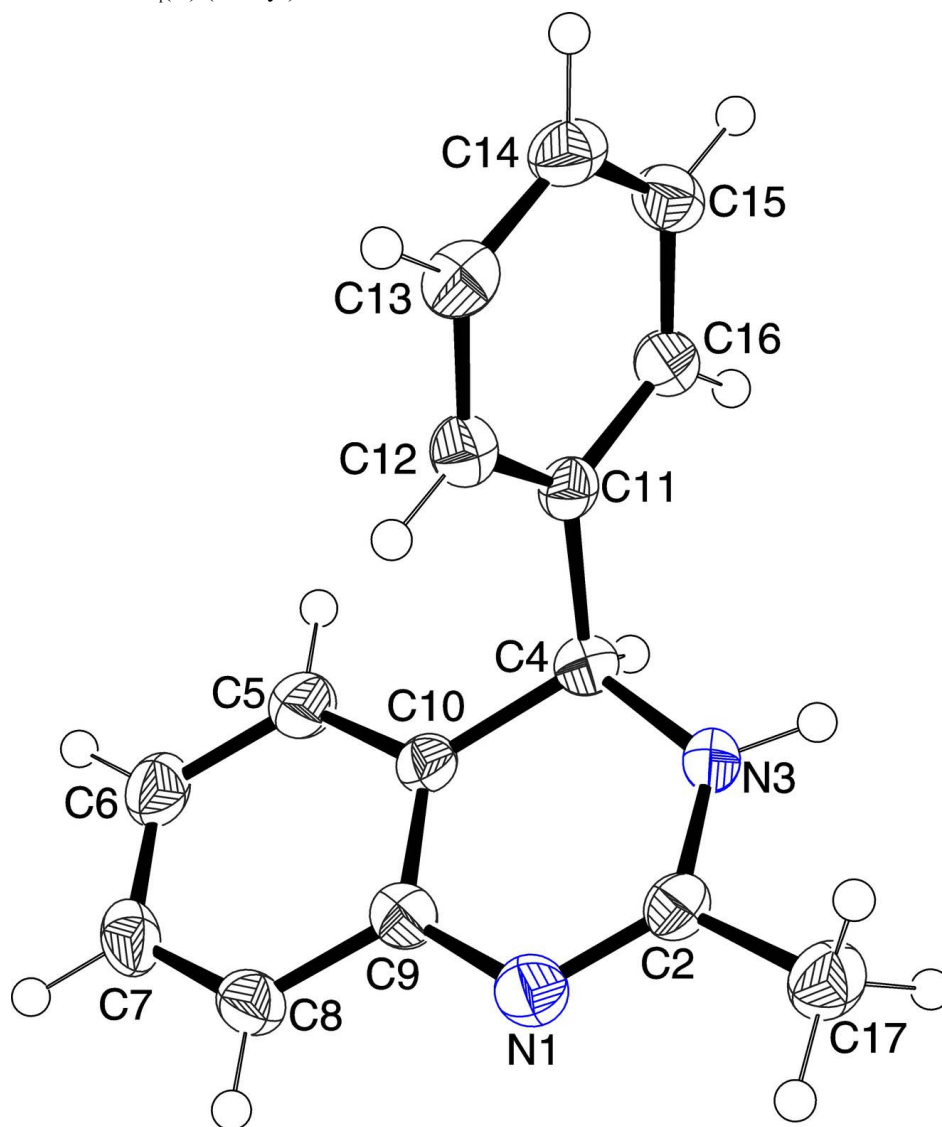times $U_{eq}(C,N)$ or 1.5 times $U_{eq}(C)$ (methyl).

Figure 1

Molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.
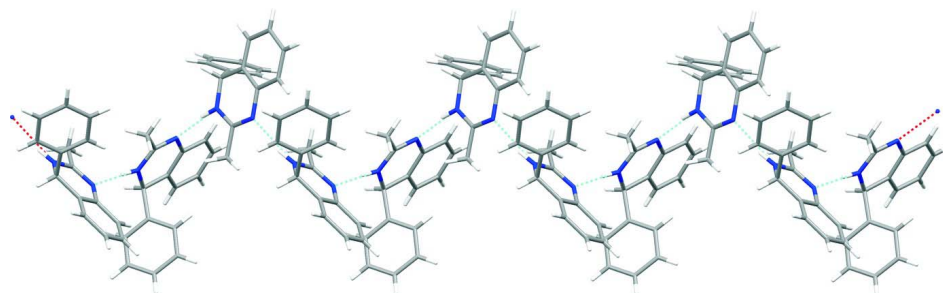
Figure 2

Part of the helical chain. Right-handed arbitrary presentation.

2-Methyl-4-phenyl-3,4-dihydroquinazoline

Crystal data

$C_{15}H_{14}N_2$	$D_x = 1.243$ Mg m^{-3}
$M_r = 222.28$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $P3_1$	Cell parameters from 3635 reflections
Hall symbol: P 31	$\theta = 0.4–28.3°$
$a = 9.5600$ (4) Å	$\mu = 0.07$ mm^{-1}
$c = 11.2569$ (5) Å	$T = 123$ K
$V = 890.97$ (7) Å^3	Long plate, colourless
$Z = 3$	$0.35 \times 0.13 \times 0.12$ mm
$F(000) = 354$	

Data collection

Bruker–Nonius KappaCCD with APEXII detector diffractometer	1468 independent reflections
	1215 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.068$
Graphite monochromator	$\theta_{max} = 28.2°$, $\theta_{min} = 2.5°$
Detector resolution: 9 pixels mm^{-1}	$h = -12 \rightarrow 12$
φ and ω scans	$k = -12 \rightarrow 12$
6729 measured reflections	$l = -12 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.046$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	
$S = 1.06$	H-atom parameters constrained
1468 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.2356P]$
155 parameters	where $P = (F_o^2 + 2F_c^2)/3$
1 restraint	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.19$ e Å^{-3}
	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
N1	−0.1844 (3)	0.2606 (3)	0.0291 (2)	0.0332 (5)
N3	−0.1137 (3)	0.4459 (3)	0.1862 (2)	0.0308 (5)

H3	−0.1520	0.4742	0.2470	0.037*
C2	−0.2197 (3)	0.3278 (3)	0.1150 (2)	0.0277 (6)
C4	0.0619 (3)	0.5311 (3)	0.1691 (2)	0.0266 (6)
H4	0.1125	0.5233	0.2447	0.032*
C5	0.2646 (3)	0.4997 (4)	0.0469 (3)	0.0339 (7)
H5	0.3474	0.5863	0.0910	0.041*
C6	0.3061 (4)	0.4266 (4)	−0.0421 (3)	0.0379 (7)
H6	0.4165	0.4634	−0.0591	0.045*
C7	0.1854 (4)	0.2994 (4)	−0.1060 (3)	0.0362 (7)
H7	0.2129	0.2484	−0.1667	0.043*
C8	0.0256 (4)	0.2473 (3)	−0.0813 (2)	0.0327 (6)
H8	−0.0563	0.1604	−0.1258	0.039*
C9	−0.0184 (3)	0.3198 (3)	0.0081 (2)	0.0281 (6)
C10	0.1033 (3)	0.4480 (3)	0.0727 (2)	0.0264 (6)
C11	0.1197 (3)	0.7087 (3)	0.1459 (2)	0.0257 (6)
C12	0.1080 (3)	0.7642 (3)	0.0349 (2)	0.0295 (6)
H12	0.0722	0.6927	−0.0311	0.035*
C13	0.1485 (3)	0.9247 (3)	0.0197 (3)	0.0341 (7)
H13	0.1425	0.9627	−0.0570	0.041*
C14	0.1977 (3)	1.0291 (4)	0.1157 (3)	0.0351 (7)
H14	0.2219	1.1376	0.1055	0.042*
C15	0.2112 (3)	0.9745 (3)	0.2266 (3)	0.0337 (6)
H15	0.2470	1.0461	0.2925	0.040*
C16	0.1724 (3)	0.8150 (3)	0.2415 (2)	0.0287 (6)
H16	0.1820	0.7781	0.3178	0.034*
C17	−0.3942 (3)	0.2713 (4)	0.1398 (3)	0.0384 (7)
H17A	−0.4623	0.1767	0.0907	0.058*
H17B	−0.4170	0.3581	0.1211	0.058*
H17C	−0.4172	0.2424	0.2239	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0291 (12)	0.0346 (13)	0.0338 (13)	0.0144 (11)	−0.0030 (10)	−0.0035 (11)
N3	0.0272 (12)	0.0290 (12)	0.0297 (12)	0.0090 (10)	0.0067 (10)	−0.0042 (10)
C2	0.0270 (14)	0.0274 (14)	0.0282 (14)	0.0131 (12)	0.0016 (11)	0.0043 (11)
C4	0.0253 (13)	0.0249 (13)	0.0282 (14)	0.0114 (11)	−0.0007 (11)	0.0003 (11)
C5	0.0275 (14)	0.0318 (15)	0.0395 (17)	0.0126 (12)	0.0032 (12)	−0.0008 (12)
C6	0.0352 (16)	0.0366 (16)	0.0451 (18)	0.0204 (14)	0.0136 (14)	0.0069 (14)
C7	0.0548 (19)	0.0348 (16)	0.0307 (15)	0.0313 (15)	0.0137 (14)	0.0080 (13)
C8	0.0410 (16)	0.0273 (14)	0.0308 (15)	0.0179 (13)	0.0017 (13)	−0.0010 (12)
C9	0.0329 (15)	0.0278 (13)	0.0264 (13)	0.0174 (12)	−0.0015 (12)	0.0014 (11)
C10	0.0276 (13)	0.0230 (13)	0.0279 (14)	0.0122 (11)	0.0036 (11)	0.0032 (11)
C11	0.0196 (12)	0.0264 (13)	0.0309 (15)	0.0113 (11)	0.0030 (10)	0.0009 (11)
C12	0.0266 (14)	0.0333 (15)	0.0297 (14)	0.0158 (12)	−0.0011 (12)	−0.0010 (12)
C13	0.0306 (15)	0.0352 (16)	0.0378 (16)	0.0175 (13)	0.0008 (12)	0.0069 (13)
C14	0.0277 (15)	0.0271 (14)	0.0511 (18)	0.0141 (12)	0.0046 (13)	0.0047 (13)
C15	0.0278 (15)	0.0312 (15)	0.0416 (16)	0.0142 (12)	−0.0011 (12)	−0.0073 (13)

| C16 | 0.0253 (13) | 0.0306 (14) | 0.0298 (15) | 0.0137 (12) | −0.0021 (11) | −0.0030 (11) |
| C17 | 0.0282 (16) | 0.0404 (17) | 0.0404 (17) | 0.0125 (13) | −0.0001 (13) | −0.0014 (13) |

Geometric parameters (Å, º)

N1—C2	1.296 (4)	C8—H8	0.9500
N1—C9	1.413 (3)	C9—C10	1.401 (4)
N3—C2	1.341 (4)	C11—C12	1.384 (4)
N3—C4	1.467 (3)	C11—C16	1.390 (4)
N3—H3	0.8800	C12—C13	1.392 (4)
C2—C17	1.500 (4)	C12—H12	0.9500
C4—C10	1.509 (4)	C13—C14	1.384 (4)
C4—C11	1.523 (3)	C13—H13	0.9500
C4—H4	1.0000	C14—C15	1.384 (4)
C5—C6	1.388 (4)	C14—H14	0.9500
C5—C10	1.394 (4)	C15—C16	1.387 (4)
C5—H5	0.9500	C15—H15	0.9500
C6—C7	1.387 (5)	C16—H16	0.9500
C6—H6	0.9500	C17—H17A	0.9800
C7—C8	1.378 (4)	C17—H17B	0.9800
C7—H7	0.9500	C17—H17C	0.9800
C8—C9	1.400 (4)		
C2—N1—C9	116.5 (2)	C5—C10—C9	119.3 (2)
C2—N3—C4	124.2 (2)	C5—C10—C4	119.9 (2)
C2—N3—H3	117.9	C9—C10—C4	120.8 (2)
C4—N3—H3	117.9	C12—C11—C16	119.2 (2)
N1—C2—N3	126.1 (2)	C12—C11—C4	121.9 (2)
N1—C2—C17	118.6 (2)	C16—C11—C4	118.6 (2)
N3—C2—C17	115.3 (2)	C11—C12—C13	120.2 (3)
N3—C4—C10	109.3 (2)	C11—C12—H12	119.9
N3—C4—C11	108.5 (2)	C13—C12—H12	119.9
C10—C4—C11	114.8 (2)	C14—C13—C12	120.4 (3)
N3—C4—H4	108.0	C14—C13—H13	119.8
C10—C4—H4	108.0	C12—C13—H13	119.8
C11—C4—H4	108.0	C15—C14—C13	119.6 (3)
C6—C5—C10	121.1 (3)	C15—C14—H14	120.2
C6—C5—H5	119.5	C13—C14—H14	120.2
C10—C5—H5	119.5	C14—C15—C16	120.0 (3)
C7—C6—C5	119.6 (3)	C14—C15—H15	120.0
C7—C6—H6	120.2	C16—C15—H15	120.0
C5—C6—H6	120.2	C15—C16—C11	120.6 (3)
C8—C7—C6	119.9 (3)	C15—C16—H16	119.7
C8—C7—H7	120.0	C11—C16—H16	119.7
C6—C7—H7	120.0	C2—C17—H17A	109.5
C7—C8—C9	121.3 (3)	C2—C17—H17B	109.5
C7—C8—H8	119.4	H17A—C17—H17B	109.5
C9—C8—H8	119.4	C2—C17—H17C	109.5

C8—C9—C10	118.9 (2)	H17A—C17—H17C	109.5
C8—C9—N1	118.5 (3)	H17B—C17—H17C	109.5
C10—C9—N1	122.6 (2)		
C9—N1—C2—N3	−1.0 (4)	N1—C9—C10—C4	−0.4 (4)
C9—N1—C2—C17	179.0 (3)	N3—C4—C10—C5	−175.0 (2)
C4—N3—C2—N1	7.2 (4)	C11—C4—C10—C5	62.8 (3)
C4—N3—C2—C17	−172.8 (3)	N3—C4—C10—C9	5.4 (3)
C2—N3—C4—C10	−8.7 (4)	C11—C4—C10—C9	−116.8 (3)
C2—N3—C4—C11	117.2 (3)	N3—C4—C11—C12	−81.0 (3)
C10—C5—C6—C7	−0.4 (4)	C10—C4—C11—C12	41.6 (3)
C5—C6—C7—C8	0.4 (4)	N3—C4—C11—C16	93.3 (3)
C6—C7—C8—C9	−0.3 (4)	C10—C4—C11—C16	−144.1 (2)
C7—C8—C9—C10	0.2 (4)	C16—C11—C12—C13	−0.1 (4)
C7—C8—C9—N1	−179.9 (2)	C4—C11—C12—C13	174.2 (2)
C2—N1—C9—C8	177.9 (3)	C11—C12—C13—C14	−1.3 (4)
C2—N1—C9—C10	−2.3 (4)	C12—C13—C14—C15	2.0 (4)
C6—C5—C10—C9	0.3 (4)	C13—C14—C15—C16	−1.3 (4)
C6—C5—C10—C4	−179.3 (3)	C14—C15—C16—C11	−0.1 (4)
C8—C9—C10—C5	−0.2 (4)	C12—C11—C16—C15	0.8 (4)
N1—C9—C10—C5	179.9 (2)	C4—C11—C16—C15	−173.7 (2)
C8—C9—C10—C4	179.4 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···N1[i]	0.88	2.04	2.908 (3)	169

Symmetry code: (i) −*y*, *x*−*y*+1, *z*+1/3.