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N-[(4-Carbamoylphenyl)carbamothioyl]-2,3,4,5-tetrafluorobenzamide

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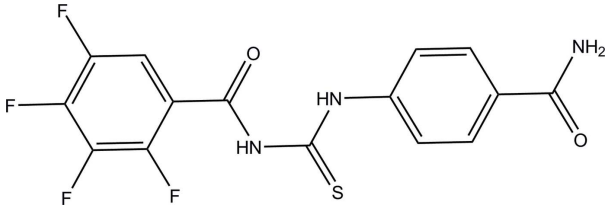
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.103; data-to-parameter ratio = 13.4.

In the title compound, $C_{15}H_9F_4N_3O_2S$, the N,N'-disubstituted thiourea fragment adopts a *cis*,*trans* geometry, stabilized by an intramolecular N—H···O hydrogen bond to the carbonyl O atom of the tetrafluorobenzoyl group. The central thiourea group makes dihedral angles of 47.79 (7) and 35.54 (8)° with the two aromatic rings. In the crystal, molecules are linked *via* N—H···O and N—H···S hydrogen bonds into two-dimensional polymeric structures parallel to (100). In turn, π–π stacking interactions between tetrafluorobenzene and benzene units [centroid–centroid distance = 3.996 (10) Å; dihedral angle = 13.60 (8)°] organize these two-dimensional assemblies into a three-dimensional framework.

Related literature

For the biological activity of thiourea derivatives, see: Zeng *et al.* (2003); Saeed *et al.* (2010). For the synthesis of thiourea derivatives, see: Nosova *et al.* (2007). For related structures, see: Saeed *et al.* (2008, 2009).



Experimental

Crystal data

$C_{15}H_9F_4N_3O_2S$ M_r = 371.31
Monoclinic, $P2_1/c$
a = 7.4246 (3) Å
b = 20.3368 (7) Å
c = 9.8954 (4) Å
β = 95.554 (3)°
V = 1487.12 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 294 K
0.38 × 0.30 × 0.26 mm

Data collection

Oxford Diffraction Xcalibur E CCD diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2006)
T_{min} = 0.860, T_{max} = 1.0
6598 measured reflections
3031 independent reflections
2263 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.103
S = 1.13
3031 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···S1^{i}	0.86	2.69	3.4861 (16)	155
N1—H1A···O1^{ii}	0.86	2.23	2.8654 (17)	130
N2—H2···O2	0.86	1.97	2.6708 (18)	138
N3—H3···O1^{iii}	0.86	2.09	2.9062 (18)	157

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); 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: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *OLEX2*.

We thank the Analytical and Testing Center of Sichuan University for the X-ray measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2335).

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supporting information

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N-[(4-Carbamoylphenyl)carbamothioyl]-2,3,4,5-tetrafluorobenzamide

Li-Dan Zhang, Chao Gao, Xue-Jiao Song and Luo-Ting Yu

S1. Comment

N-(4-Carbamoylphenylcarbamothioyl)-2,3,4,5-tetrafluorobenzamide derivatives are of great importance owing to their interesting biological properties (Zeng *et al.*, 2003; Saeed *et al.*, 2010). The title compound is one of the key intermediates in our synthetic route to antiviral drugs. We report here its crystal structure.

In the title compound, $C_{15}H_9F_4N_3O_2S$, (Fig.1), the *cis,trans* geometry of the thiourea moiety is stabilized by intramolecular N2—H2···O2 and N3—H3···F1 hydrogen bonds. The central thiourea group makes dihedral angles of 47.79 (7) and 35.54 (8)° with the benzamide unit and the fluorobenzene ring, respectively. A combination of intermolecular π–π stacking interactions, N—H···O, N—H···F and N—H···S hydrogen bonds helps to stabilize the crystal structure (Table 1 and Fig.2).

S2. Experimental

A solution of 0.23 g (3 mmol) of ammonium thiocyanate in 7 ml of acetonitrile was added to a solution of 0.64 g (3 mmol) of 2,3,4,5-tetrafluorobenzoyl chloride in 2.5 ml of toluene. The mixture was heated for 5 min at 40°C and filtered from ammonium chloride, the filtrate was added to a solution of 0.32 g (3 mmol) of 4-aminobenzamide in 5 ml of acetonitrile, the mixture was stirred for 2 h at room temperature and evaporated, and the residue was washed with ethanol and recrystallized from ethanol. Yield 0.91 g (82%). Crystals suitable for X-ray analysis were obtained by slow evaporation from ethyl acetate solution.

S3. Refinement

All H atoms were positioned geometrically (C—H = 0.93 Å, N—H = 0.86 Å) and refined using a riding model approximation with U_{iso}(H) = 1.2U_{eq}(C,*N*).

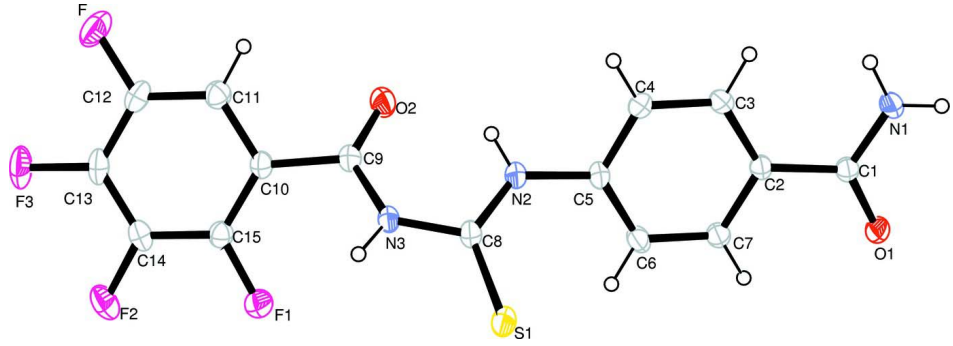

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

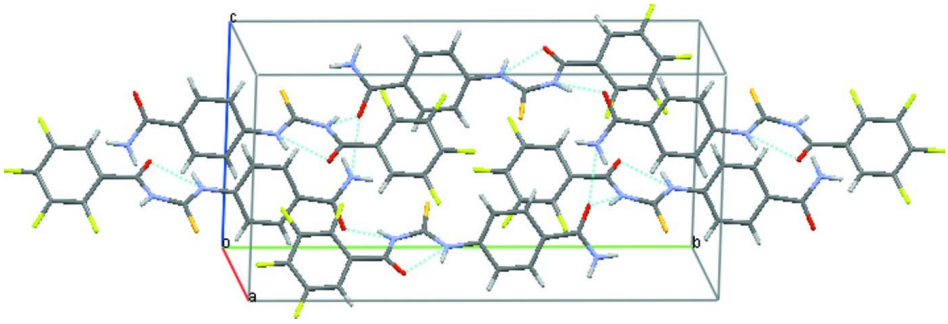

Figure 2

A packing diagram of the title compound, showing classical hydrogen bonds of N1—H1A···O1, N2—H2···O2 and N3—H3···O1 as green dashed lines.

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Crystal data

$C_{15}H_9F_4N_3O_2S$
$M_r = 371.31$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.4246$ (3) Å
$b = 20.3368$ (7) Å
$c = 9.8954$ (4) Å
$\beta = 95.554$ (3)°
$V = 1487.12$ (9) Å^3
$Z = 4$
$F(000) = 752$
$D_x = 1.658$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
Cell parameters from 3669 reflections
$\theta = 3.3$–$29.2°$
$\mu = 0.28$ mm^{-1}
$T = 294$ K
Block, colourless
0.38 × 0.30 × 0.26 mm

Data collection

Oxford Diffraction Xcalibur E CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0874 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2006)
$T_{min} = 0.860$, $T_{max} = 1.0$
6598 measured reflections
3031 independent reflections
2263 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.4°$
$h = -9 \rightarrow 9$
$k = -25 \rightarrow 21$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.103$
$S = 1.13$
3031 reflections
226 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
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.41600 (7)	0.40876 (2)	0.28889 (6)	0.05125 (18)
F	0.98701 (18)	0.10215 (6)	−0.07009 (12)	0.0623 (4)
F1	0.66951 (14)	0.21050 (5)	0.34645 (9)	0.0445 (3)
F2	0.72451 (16)	0.08149 (5)	0.33952 (12)	0.0543 (3)
F3	0.87569 (17)	0.02540 (5)	0.12899 (13)	0.0635 (4)
O1	0.66762 (17)	0.73716 (6)	0.33958 (11)	0.0386 (3)
O2	0.91223 (18)	0.33325 (6)	0.09914 (14)	0.0471 (3)
N1	0.7405 (2)	0.75363 (7)	0.12865 (14)	0.0434 (4)
H1B	0.7340	0.7956	0.1382	0.052*
H1A	0.7683	0.7373	0.0532	0.052*
N2	0.7175 (2)	0.43553 (7)	0.17165 (14)	0.0390 (4)
H2	0.8046	0.4200	0.1300	0.047*
N3	0.64026 (19)	0.32604 (7)	0.18763 (14)	0.0356 (3)
H3	0.5580	0.2981	0.2036	0.043*
C1	0.7076 (2)	0.71401 (8)	0.23066 (16)	0.0304 (4)
C2	0.7164 (2)	0.64135 (8)	0.21097 (16)	0.0286 (4)
C3	0.7548 (3)	0.61151 (9)	0.09123 (18)	0.0392 (4)
H3A	0.7823	0.6372	0.0182	0.047*
C4	0.7524 (3)	0.54374 (9)	0.07970 (18)	0.0425 (5)
H4	0.7771	0.5241	−0.0013	0.051*
C5	0.7133 (2)	0.50499 (8)	0.18833 (17)	0.0343 (4)
C6	0.6795 (2)	0.53412 (8)	0.30877 (17)	0.0367 (4)
H6	0.6566	0.5083	0.3828	0.044*
C7	0.6796 (2)	0.60191 (8)	0.31958 (16)	0.0329 (4)
H7	0.6546	0.6214	0.4007	0.039*
C8	0.6006 (2)	0.39170 (8)	0.21371 (17)	0.0345 (4)
C9	0.7920 (2)	0.30012 (9)	0.14025 (17)	0.0338 (4)
C10	0.8043 (2)	0.22623 (8)	0.14010 (16)	0.0315 (4)
C11	0.8887 (2)	0.19686 (9)	0.03581 (18)	0.0369 (4)
H11	0.9315	0.2228	−0.0316	0.044*
C12	0.9089 (2)	0.13022 (9)	0.03208 (19)	0.0410 (4)
C13	0.8521 (3)	0.09051 (8)	0.1325 (2)	0.0414 (5)
C14	0.7735 (2)	0.11852 (8)	0.23825 (18)	0.0369 (4)
C15	0.7476 (2)	0.18583 (8)	0.24020 (16)	0.0326 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0543 (3)	0.0289 (3)	0.0750 (4)	0.0028 (2)	0.0295 (3)	−0.0031 (2)
F	0.0717 (9)	0.0532 (7)	0.0638 (8)	0.0202 (6)	0.0162 (6)	−0.0171 (6)
F1	0.0550 (7)	0.0402 (6)	0.0394 (6)	0.0026 (5)	0.0093 (5)	0.0001 (5)
F2	0.0617 (8)	0.0366 (6)	0.0643 (7)	−0.0022 (5)	0.0052 (6)	0.0184 (5)
F3	0.0688 (8)	0.0237 (6)	0.0975 (10)	0.0083 (5)	0.0051 (7)	−0.0067 (6)
O1	0.0568 (8)	0.0293 (7)	0.0305 (6)	0.0036 (6)	0.0085 (6)	−0.0027 (5)
O2	0.0453 (8)	0.0312 (7)	0.0677 (9)	−0.0037 (6)	0.0199 (7)	0.0007 (6)
N1	0.0702 (11)	0.0250 (8)	0.0374 (8)	−0.0013 (7)	0.0174 (8)	0.0019 (7)
N2	0.0480 (9)	0.0228 (7)	0.0488 (9)	−0.0001 (7)	0.0181 (7)	−0.0001 (7)
N3	0.0392 (8)	0.0215 (7)	0.0481 (9)	0.0008 (6)	0.0145 (7)	0.0009 (6)
C1	0.0333 (9)	0.0274 (9)	0.0303 (9)	0.0002 (7)	0.0031 (7)	0.0003 (7)
C2	0.0310 (9)	0.0245 (9)	0.0303 (8)	0.0002 (7)	0.0028 (7)	0.0005 (7)
C3	0.0559 (12)	0.0280 (9)	0.0359 (10)	−0.0041 (8)	0.0166 (9)	0.0013 (8)
C4	0.0614 (12)	0.0293 (10)	0.0398 (10)	−0.0009 (9)	0.0206 (9)	−0.0057 (8)
C5	0.0409 (10)	0.0213 (9)	0.0416 (10)	−0.0004 (7)	0.0075 (8)	0.0002 (7)
C6	0.0509 (11)	0.0273 (9)	0.0319 (9)	−0.0022 (8)	0.0037 (8)	0.0056 (7)
C7	0.0432 (10)	0.0288 (9)	0.0269 (8)	−0.0004 (7)	0.0042 (7)	−0.0007 (7)
C8	0.0434 (10)	0.0233 (9)	0.0371 (9)	0.0023 (7)	0.0060 (8)	0.0010 (7)
C9	0.0368 (10)	0.0271 (9)	0.0377 (9)	0.0016 (7)	0.0045 (7)	0.0004 (7)
C10	0.0310 (9)	0.0252 (9)	0.0380 (9)	0.0018 (7)	0.0015 (7)	−0.0003 (7)
C11	0.0342 (9)	0.0341 (10)	0.0426 (10)	0.0040 (8)	0.0043 (8)	0.0013 (8)
C12	0.0387 (10)	0.0364 (10)	0.0475 (11)	0.0104 (8)	0.0022 (8)	−0.0113 (9)
C13	0.0389 (10)	0.0221 (9)	0.0612 (12)	0.0040 (8)	−0.0061 (9)	−0.0046 (9)
C14	0.0350 (10)	0.0275 (9)	0.0469 (10)	−0.0027 (7)	−0.0032 (8)	0.0060 (8)
C15	0.0296 (9)	0.0313 (9)	0.0366 (9)	0.0018 (7)	0.0022 (7)	−0.0011 (8)

Geometric parameters (Å, º)

S1—C8	1.6583 (18)	C2—C7	1.389 (2)
F—C12	1.341 (2)	C3—H3A	0.9300
F1—C15	1.3458 (18)	C3—C4	1.383 (2)
F2—C14	1.332 (2)	C4—H4	0.9300
F3—C13	1.3365 (18)	C4—C5	1.386 (2)
O1—C1	1.2383 (18)	C5—C6	1.376 (2)
O2—C9	1.219 (2)	C6—H6	0.9300
N1—H1B	0.8600	C6—C7	1.383 (2)
N1—H1A	0.8600	C7—H7	0.9300
N1—C1	1.333 (2)	C9—C10	1.505 (2)
N2—H2	0.8600	C10—C11	1.393 (2)
N2—C5	1.423 (2)	C10—C15	1.384 (2)
N2—C8	1.338 (2)	C11—H11	0.9300
N3—H3	0.8600	C11—C12	1.364 (2)
N3—C8	1.397 (2)	C12—C13	1.378 (3)
N3—C9	1.367 (2)	C13—C14	1.370 (3)
C1—C2	1.493 (2)	C14—C15	1.383 (2)

C2—C3	1.385 (2)		
F—C12—C11	119.99 (18)	C4—C3—H3A	119.8
F—C12—C13	118.62 (16)	C4—C5—N2	117.77 (15)
F1—C15—C10	121.45 (14)	C5—N2—H2	116.5
F1—C15—C14	116.81 (15)	C5—C4—H4	119.8
F2—C14—C13	120.47 (15)	C5—C6—H6	120.1
F2—C14—C15	120.04 (16)	C5—C6—C7	119.84 (15)
F3—C13—C12	120.80 (18)	C6—C5—N2	122.40 (15)
F3—C13—C14	119.87 (18)	C6—C5—C4	119.77 (15)
O1—C1—N1	120.43 (15)	C6—C7—C2	120.96 (15)
O1—C1—C2	120.47 (14)	C6—C7—H7	119.5
O2—C9—N3	123.76 (16)	C7—C2—C1	117.15 (14)
O2—C9—C10	120.32 (15)	C7—C6—H6	120.1
N1—C1—C2	119.09 (14)	C8—N2—H2	116.5
H1B—N1—H1A	120.0	C8—N2—C5	127.09 (15)
N2—C8—S1	126.10 (13)	C8—N3—H3	115.6
N2—C8—N3	115.14 (15)	C9—N3—H3	115.6
N3—C8—S1	118.75 (12)	C9—N3—C8	128.85 (14)
N3—C9—C10	115.92 (14)	C10—C11—H11	119.9
C1—N1—H1B	120.0	C11—C10—C9	117.41 (15)
C1—N1—H1A	120.0	C11—C12—C13	121.38 (17)
C2—C3—H3A	119.8	C12—C11—C10	120.29 (17)
C2—C7—H7	119.5	C12—C11—H11	119.9
C3—C2—C1	124.10 (15)	C13—C14—C15	119.49 (16)
C3—C2—C7	118.74 (15)	C14—C13—C12	119.32 (15)
C3—C4—H4	119.8	C14—C15—C10	121.71 (15)
C3—C4—C5	120.31 (16)	C15—C10—C9	124.72 (15)
C4—C3—C2	120.34 (16)	C15—C10—C11	117.75 (15)
F—C12—C13—F3	0.6 (3)	C5—N2—C8—N3	−178.02 (15)
F—C12—C13—C14	179.40 (16)	C5—C6—C7—C2	−1.1 (3)
F2—C14—C15—F1	−1.0 (2)	C7—C2—C3—C4	1.4 (3)
F2—C14—C15—C10	177.00 (15)	C8—N2—C5—C4	−138.63 (19)
F3—C13—C14—F2	1.7 (3)	C8—N2—C5—C6	44.1 (3)
F3—C13—C14—C15	−179.20 (15)	C8—N3—C9—O2	−8.1 (3)
O1—C1—C2—C3	178.02 (16)	C8—N3—C9—C10	172.27 (16)
O1—C1—C2—C7	−0.5 (2)	C9—N3—C8—S1	−172.62 (14)
O2—C9—C10—C11	−33.5 (2)	C9—N3—C8—N2	8.7 (3)
O2—C9—C10—C15	142.48 (18)	C9—C10—C11—C12	178.10 (15)
N1—C1—C2—C3	−0.9 (3)	C9—C10—C15—F1	2.2 (2)
N1—C1—C2—C7	−179.44 (15)	C9—C10—C15—C14	−175.74 (15)
N2—C5—C6—C7	179.11 (16)	C10—C11—C12—F	178.65 (16)
N3—C9—C10—C11	146.16 (16)	C10—C11—C12—C13	−2.0 (3)
N3—C9—C10—C15	−37.9 (2)	C11—C10—C15—F1	178.11 (14)
C1—C2—C3—C4	−177.14 (16)	C11—C10—C15—C14	0.2 (2)
C1—C2—C7—C6	178.11 (16)	C11—C12—C13—F3	−178.74 (16)
C2—C3—C4—C5	−0.6 (3)	C11—C12—C13—C14	0.1 (3)

C3—C2—C7—C6	−0.5 (3)	C12—C13—C14—F2	−177.14 (15)
C3—C4—C5—N2	−178.38 (17)	C12—C13—C14—C15	2.0 (3)
C3—C4—C5—C6	−1.0 (3)	C13—C14—C15—F1	179.87 (15)
C4—C5—C6—C7	1.9 (3)	C13—C14—C15—C10	−2.1 (3)
C5—N2—C8—S1	3.4 (3)	C15—C10—C11—C12	1.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···S1^{i}	0.86	2.69	3.4861 (16)	155
N1—H1*A*···O1^{ii}	0.86	2.23	2.8654 (17)	130
N2—H2···O2	0.86	1.97	2.6708 (18)	138
N3—H3···F1	0.86	2.37	2.8234 (17)	113
N3—H3···O1^{iii}	0.86	2.09	2.9062 (18)	157

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*, −*y*+3/2, *z*−1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2.