organic compounds

(E)-1-(4-Fluorophenyl)ethan-1-one semicarbazone

Hoong-Kun Fun,[a]*‡ Chin Sing Yeap,[a]§ Mahesh Padaki,[b] Shridhar Malladi[b] and Arun M. Isloor[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Department of Chemistry, National Institute of Technology–Karnataka, Surathkal, Mangalore 575 025, India
Correspondence e-mail: hkfun@usm.my

In the title compound, $C_9H_{10}FN_3O$, the semicarbazone group is nearly planar, with the maximum deviation of 0.044 (1) Å for one of the N atoms. The mean plane of semicarbazone group forms a dihedral angle of 30.94 (4)° with the benzene ring. The molecules are linked into a supramolecular chain by N—H···O hydrogen bonds formed along the c axis. The crystal structure is further stabilized by weak intermolucular C—H···π interactions; the closest C···Cg contact is 3.6505 (11) Å.

Related literature

For hydrogen-bond motifs, see: Bernstein et al. (1995). For applications of semicarbazone derivatives, see: Chandra & Gupta (2005); Jain et al. (2002); Pilgram (1978); Warren et al. (1977); Yogeeswari et al. (2004). For the preparation of the compound, see: Furniss et al. (1978). For related structures, see: Fun et al. (2009a,b). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).
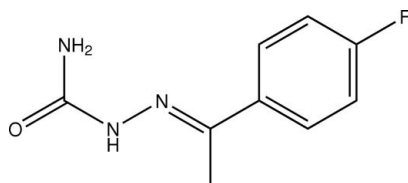
Experimental

Crystal data

$C_9H_{10}FN_3O$	Monoclinic, $P2_1/c$
$M_r = 195.20$	$a = 18.8207$ (3) Å
$b = 6.6387$ (1) Å	Mo $K\alpha$ radiation
$c = 7.3074$ (1) Å	$\mu = 0.11$ mm^{-1}
$\beta = 95.887$ (1)°	$T = 100$ K
$V = 908.21$ (2) Å^3	$0.30 \times 0.10 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	17523 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	3998 independent reflections
$T_{min} = 0.876$, $T_{max} = 0.991$	2766 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.151$	
$S = 1.07$	
3998 reflections	$\Delta\rho_{max} = 0.51$ e Å^{-3}
167 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N2···O1[i]	0.96 (2)	1.94 (2)	2.8998 (11)	179.2 (18)
N3—H2N3···O1[ii]	0.82 (2)	2.07 (2)	2.8901 (12)	176 (2)
C2—H2A···Cg1[iii]	0.989 (17)	2.927 (18)	3.7250 (12)	138.5 (12)
C5—H5A···Cg1[iv]	0.976 (14)	2.825 (13)	3.6505 (11)	142.8 (10)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+1, -z+2$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x, -y-\frac{1}{2}, z-\frac{3}{2}$. $Cg1$ is the centroid of C1–C6 benzene ring.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. **34**, 1555–1573.
Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Chandra, S. & Gupta, L. K. (2005). Spectrochim. Acta Part A, **62**, 1089–1094.
Cosier, J. & Glazer, A. M. (1986). J. Appl. Cryst. **19**, 105–107.
Fun, H.-K., Chantrapromma, S., Sujith, K. V. & Kalluraya, B. (2009a). Acta Cryst. E**65**, o445.
Fun, H.-K., Goh, J. H., Padaki, M., Malladi, S. & Isloor, A. M. (2009b). Acta Cryst. E**65**, o1591.
Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. & Tatchell, A. R. (1978). Vogel's Textbook of Practical Organic Chemistry, 4th ed., p. 1112. London: ELBS.

‡ Thomson Reuters ResearcherID: A-3561-2009.
§ Thomson Reuters ResearcherID: A-5523-2009.

organic compounds

Jain, V. K., Handa, A., Pandya, R., Shrivastav, P. & Agrawal, Y. K. (2002). *React. Funct. Polym.* **51**, 101–110.

Pilgram, K. H. G. (1978). US Patent No. 4 108 399.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Warren, J. D., Woodward, D. L. & Hargreaves, R. T. (1977). *J. Med. Chem.* **20**, 1520–1521.

Yogeeswari, P., Sriram, D., Pandeya, S. N. & Stables, J. P. (2004). *Farmaco*, **59**, 609–613.

supporting information

(*E*)-1-(4-Fluorophenyl)ethan-1-one semicarbazone

Hoong-Kun Fun, Chin Sing Yeap, Mahesh Padaki, Shridhar Malladi and Arun M. Isloor

S1. Comment

In organic chemistry, a semicarbazone is a derivative of an aldehyde or ketone formed by a condensation between a ketone or aldehyde and semicarbazide. Semicarbazones find a large number of applications in the field of synthetic chemistry, such as in medicinal chemistry (Warren *et al.*, 1977), organometallics (Chandra & Gupta, 2005), polymers (Jain *et al.*, 2002), and herbicides (Pilgram, 1978). 4-Sulphamoylphenyl semicarbazones were found to possess anti-convulsant activity (Yogeeswari *et al.*, 2004). We hereby report the crystal structure of a semicarbazone of commercial importance, (I).

The bond lengths and angles for (I), Fig. 1, are comparable to those found in related structures (Fun *et al.*, 2009a, b). A maximum deviation of 0.044 (1) Å for atom N2 from the mean plane formed by atoms O1, N1, N2, N3, C6, C7, C8 and C9, indicates that the semicarbazone group is nearly planar. This mean plane makes a dihedral angle of 30.94 (4)° with the C1–C6 benzene ring. The molecules are linked into one-dimensional chains by intermolecular N—H···O hydrogen bonds along the *c* axis (Fig. 2); these hydrogen bonding interactions generate $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995). The crystal structure is stabilized by weak intermolecular C—H···π interactions (Table 1).

S2. Experimental

Semicarbazide hydrochloride (0.86 g, 7.70 mmol) and freshly recrystallized sodium acetate (0.77 g, 9.40 mmol) were dissolved in water (10 ml) following a literature procedure (Furniss *et al.*, 1978). The reaction mixture was stirred at room temperature for 10 minutes. To this, 4-fluoroacetophenone (1.00 g, 7.23 mmol) was added and the mixture was shaken well. A little alcohol was added to dissolve the turbidity. The mixture was shaken for a further 10 minutes and allowed to stand. The title compound (I) crystallizes on standing for 6 h. The separated crystals were filtered, washed with cold water and recrystallized from ethanol. Yield: 1.34 g (95%). M.p. 485-486 K.

S3. Refinement

All hydrogen atoms were located from the difference Fourier map and refined freely, N—H = 0.820 (19) - 0.957 (19) Å and C–H = 0.945 (19) - 1.005 (18) Å.
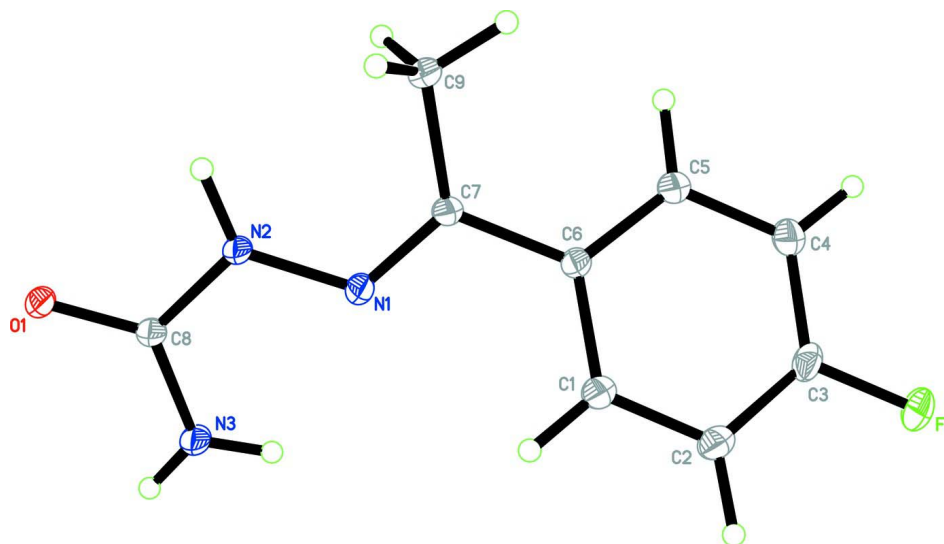
Figure 1

The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.
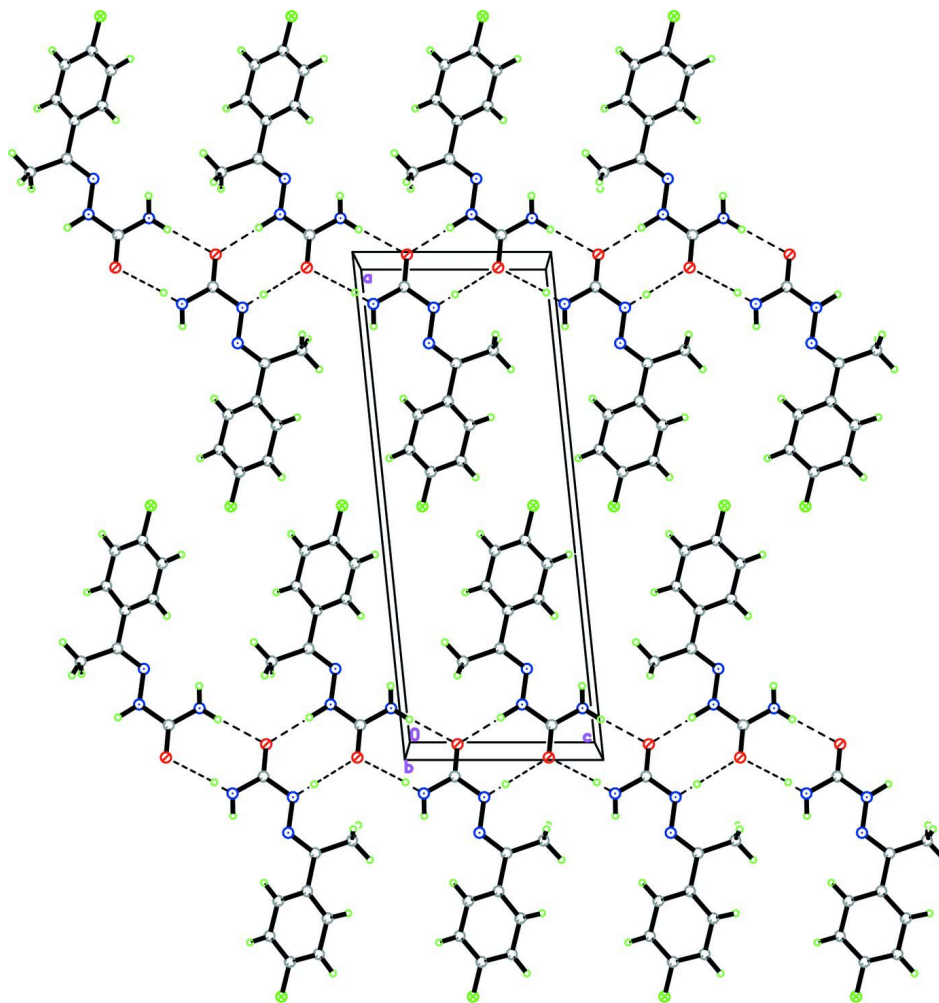
Figure 2

The crystal packing of (I), viewed down the *b* axis, showing the molecules are linked along the *c* axis. Hydrogen bonds are shown in as dashed lines.

(*E*)-1-(4-Fluorophenyl)ethan-1-one semicarbazone

Crystal data

$C_9H_{10}FN_3O$	$F(000) = 408$
$M_r = 195.20$	$D_x = 1.428$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5018 reflections
$a = 18.8207$ (3) Å	$\theta = 4.2$–$38.8°$
$b = 6.6387$ (1) Å	$\mu = 0.11$ mm^{-1}
$c = 7.3074$ (1) Å	$T = 100$ K
$\beta = 95.887$ (1)°	Needle, colourless
$V = 908.21$ (2) Å^3	$0.30 \times 0.10 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	17523 measured reflections
	3998 independent reflections
Radiation source: fine-focus sealed tube	2766 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.033$
φ and ω scans	$\theta_{max} = 35.0°$, $\theta_{min} = 1.1°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -29 \rightarrow 30$
	$k = -10 \rightarrow 10$
$T_{min} = 0.876$, $T_{max} = 0.991$	$l = -7 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.151$	
$S = 1.07$	H atoms treated by a mixture of independent and constrained refinement
3998 reflections	
167 parameters	$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.1557P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.51$ e Å^{-3}
	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

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	$U_{iso}*/U_{eq}$
F1	0.50077 (4)	0.48694 (11)	0.79001 (10)	0.02274 (17)
O1	−0.01336 (4)	0.50372 (12)	0.73484 (10)	0.01547 (16)
N1	0.16753 (5)	0.50702 (12)	0.66798 (11)	0.01257 (16)
N2	0.09495 (5)	0.50670 (13)	0.62389 (11)	0.01339 (17)
N3	0.08724 (5)	0.50728 (15)	0.93755 (12)	0.01734 (19)
C1	0.31185 (5)	0.59520 (16)	0.76477 (14)	0.01595 (19)
C2	0.38374 (6)	0.59368 (17)	0.82935 (14)	0.0178 (2)
C3	0.43028 (5)	0.49203 (16)	0.72738 (15)	0.01591 (19)
C4	0.40812 (6)	0.39453 (17)	0.56461 (14)	0.0177 (2)
C5	0.33579 (5)	0.39948 (17)	0.50051 (13)	0.01569 (19)
C6	0.28652 (5)	0.49812 (14)	0.60026 (13)	0.01153 (17)
C7	0.20888 (5)	0.49673 (14)	0.53803 (13)	0.01158 (17)
C8	0.05269 (5)	0.50588 (15)	0.76711 (13)	0.01249 (18)
C9	0.18228 (6)	0.48336 (16)	0.33718 (13)	0.01471 (19)

H1A	0.2783 (8)	0.667 (2)	0.8362 (19)	0.023 (4)*
H2A	0.4017 (8)	0.666 (3)	0.943 (2)	0.031 (4)*
H4A	0.4422 (7)	0.324 (2)	0.4966 (19)	0.021 (3)*
H5A	0.3214 (7)	0.328 (2)	0.3860 (19)	0.017 (3)*
H9A	0.1565 (9)	0.602 (3)	0.303 (2)	0.035 (4)*
H9B	0.1536 (9)	0.364 (3)	0.317 (2)	0.037 (5)*
H9C	0.2216 (10)	0.480 (2)	0.254 (2)	0.031 (5)*
H1N2	0.0681 (10)	0.502 (2)	0.505 (3)	0.029 (4)*
H1N3	0.1329 (10)	0.506 (2)	0.947 (2)	0.025 (4)*
H2N3	0.0643 (10)	0.505 (2)	1.027 (3)	0.030 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0096 (3)	0.0346 (4)	0.0230 (3)	0.0012 (2)	−0.0031 (2)	−0.0014 (3)
O1	0.0103 (3)	0.0256 (4)	0.0103 (3)	−0.0002 (3)	0.0004 (2)	−0.0005 (3)
N1	0.0098 (3)	0.0167 (4)	0.0110 (3)	0.0002 (3)	0.0002 (3)	0.0005 (3)
N2	0.0101 (3)	0.0220 (4)	0.0080 (3)	−0.0003 (3)	0.0004 (3)	0.0000 (3)
N3	0.0120 (4)	0.0317 (5)	0.0082 (3)	−0.0002 (3)	0.0003 (3)	−0.0006 (3)
C1	0.0137 (4)	0.0188 (5)	0.0150 (4)	0.0013 (4)	−0.0002 (3)	−0.0034 (3)
C2	0.0152 (4)	0.0214 (5)	0.0161 (4)	0.0001 (4)	−0.0022 (3)	−0.0036 (4)
C3	0.0097 (4)	0.0205 (5)	0.0169 (4)	0.0002 (3)	−0.0017 (3)	0.0026 (3)
C4	0.0131 (4)	0.0230 (5)	0.0173 (4)	0.0029 (4)	0.0021 (3)	−0.0016 (4)
C5	0.0134 (4)	0.0202 (5)	0.0133 (4)	0.0012 (3)	0.0006 (3)	−0.0024 (3)
C6	0.0107 (4)	0.0134 (4)	0.0103 (4)	0.0005 (3)	0.0002 (3)	0.0007 (3)
C7	0.0116 (4)	0.0128 (4)	0.0102 (4)	0.0005 (3)	0.0003 (3)	−0.0006 (3)
C8	0.0114 (4)	0.0167 (4)	0.0094 (4)	0.0000 (3)	0.0009 (3)	−0.0005 (3)
C9	0.0122 (4)	0.0211 (5)	0.0105 (4)	−0.0010 (4)	−0.0003 (3)	−0.0006 (3)

Geometric parameters (Å, º)

F1—C3	1.3587 (12)	C2—C3	1.3826 (15)
O1—C8	1.2413 (12)	C2—H2A	0.989 (17)
N1—C7	1.2900 (13)	C3—C4	1.3805 (15)
N1—N2	1.3709 (12)	C4—C5	1.3939 (14)
N2—C8	1.3779 (13)	C4—H4A	0.971 (14)
N2—H1N2	0.957 (19)	C5—C6	1.3995 (14)
N3—C8	1.3446 (13)	C5—H5A	0.976 (14)
N3—H1N3	0.856 (18)	C6—C7	1.4851 (13)
N3—H2N3	0.820 (19)	C7—C9	1.5040 (13)
C1—C2	1.3866 (14)	C9—H9A	0.945 (19)
C1—C6	1.4037 (14)	C9—H9B	0.964 (18)
C1—H1A	0.983 (14)	C9—H9C	1.005 (18)
C7—N1—N2	119.27 (8)	C4—C5—C6	120.83 (9)
N1—N2—C8	117.41 (8)	C4—C5—H5A	116.8 (8)
N1—N2—H1N2	129.3 (10)	C6—C5—H5A	122.3 (8)
C8—N2—H1N2	113.3 (10)	C5—C6—C1	118.42 (9)

C8—N3—H1N3	117.6 (12)	C5—C6—C7	121.42 (8)
C8—N3—H2N3	119.6 (13)	C1—C6—C7	120.14 (8)
H1N3—N3—H2N3	122.7 (18)	N1—C7—C6	115.04 (8)
C2—C1—C6	121.47 (9)	N1—C7—C9	123.77 (9)
C2—C1—H1A	118.7 (8)	C6—C7—C9	121.19 (8)
C6—C1—H1A	119.8 (8)	O1—C8—N3	123.76 (9)
C3—C2—C1	118.04 (9)	O1—C8—N2	120.04 (9)
C3—C2—H2A	120.6 (9)	N3—C8—N2	116.20 (9)
C1—C2—H2A	121.4 (9)	C7—C9—H9A	108.5 (11)
F1—C3—C4	118.48 (9)	C7—C9—H9B	108.7 (10)
F1—C3—C2	118.77 (9)	H9A—C9—H9B	112.6 (16)
C4—C3—C2	122.75 (10)	C7—C9—H9C	113.6 (11)
C3—C4—C5	118.48 (10)	H9A—C9—H9C	104.5 (14)
C3—C4—H4A	120.7 (8)	H9B—C9—H9C	109.0 (14)
C5—C4—H4A	120.8 (8)		
C7—N1—N2—C8	176.26 (9)	C2—C1—C6—C7	177.96 (9)
C6—C1—C2—C3	−0.43 (16)	N2—N1—C7—C6	179.99 (8)
C1—C2—C3—F1	−179.17 (10)	N2—N1—C7—C9	−0.23 (14)
C1—C2—C3—C4	0.56 (17)	C5—C6—C7—N1	150.01 (10)
F1—C3—C4—C5	179.90 (9)	C1—C6—C7—N1	−28.31 (13)
C2—C3—C4—C5	0.17 (17)	C5—C6—C7—C9	−29.77 (14)
C3—C4—C5—C6	−1.05 (16)	C1—C6—C7—C9	151.91 (10)
C4—C5—C6—C1	1.16 (15)	N1—N2—C8—O1	−179.35 (9)
C4—C5—C6—C7	−177.18 (9)	N1—N2—C8—N3	0.57 (13)
C2—C1—C6—C5	−0.41 (15)		

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H1*N2*⋯O1[i]	0.96 (2)	1.94 (2)	2.8998 (11)	179.2 (18)
N3—H2*N3*⋯O1[ii]	0.82 (2)	2.07 (2)	2.8901 (12)	176 (2)
C2—H2*A*⋯*Cg*1[iii]	0.989 (17)	2.927 (18)	3.7250 (12)	138.5 (12)
C5—H5*A*⋯*Cg*1[iv]	0.976 (14)	2.825 (13)	3.6505 (11)	142.8 (10)

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