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4-(3-Fluorophenyl)-1-(propan-2-ylidene)-thiosemicarbazone

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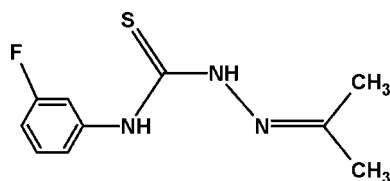
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.068; wR factor = 0.217; data-to-parameter ratio = 14.1.

The title compound, $\text{C}_{10}\text{H}_{12}\text{FN}_3\text{S}$, crystallizes in the same space group ($P2_1/c$) as two polymorphic forms of 4-phenyl-1-(propan-2-ylidene)thiosemicarbazone [Jian *et al.* (2005). *Acta Cryst. E61*, o653–o654; Venkatraman *et al.* (2005). *Acta Cryst. E61*, o3914–o3916]. The arrangement of molecules relative to the twofold screw axes is similar to that in the crystal structure of the lower density polymorph. In the solid state, the molecular conformation is stabilized by an intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond. The molecules form centrosymmetric $R_2^2(8)$ dimers in the crystal through pairs of $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

Related literature

For related structures, see: Basu & Das (2011); Park & Ahn (1985); Parsons *et al.* (2000); Jian *et al.* (2005); Venkatraman *et al.* (2005). For description of the Cambridge Structural Database, see: Allen (2002). For the antitumor, antiviral and antifungal activity of thiosemicarbazones, see: Kalinowski *et al.* (2009); Smee & Sidwell (2003); Beraldo & Gambino (2004). For their metal-chelating properties, see: Paterson & Donnelly (2011); Casas *et al.* (2000).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_{12}\text{FN}_3\text{S}$
 $M_r = 225.29$
 Monoclinic, $P2_1/c$
 $a = 9.038$ (2) Å
 $b = 10.515$ (2) Å
 $c = 11.869$ (2) Å

 $\beta = 99.77$ (3)°
 $V = 1111.6$ (4) Å³
 $Z = 4$
 Cu $K\alpha$ radiation

 $\mu = 2.48$ mm⁻¹
 $T = 296$ K
 $0.55 \times 0.30 \times 0.10$ mm

Data collection

 Kuma KM-4 diffractometer
 Absorption correction: for a cylinder mounted on the φ axis (Dwiggins, 1975)
 $T_{\min} = 0.435$, $T_{\max} = 0.485$
 3800 measured reflections

 1942 independent reflections
 1252 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.084$
 3 standard reflections every 100 reflections
 intensity decay: 3.3%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.217$
 $S = 1.04$
 1942 reflections

 138 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N3}$	0.86	2.12	2.553 (5)	111
$\text{N2}-\text{H2}\cdots\text{S1}^i$	0.86	2.67	3.465 (3)	154

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

Data collection: *KM-4 Software* (Kuma Diffraction, 1991); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999), *Mercury* (Macrae *et al.*, 2006) and *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2024).

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supporting information

Acta Cryst. (2011). E67, o3010 [doi:10.1107/S1600536811042504]

4-(3-Fluorophenyl)-1-(propan-2-ylidene)thiosemicarbazone

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S1. Comment

Thiosemicarbazones are widely studied due to their antitumor, antiviral and antifungal activity (Kalinowski *et al.*, 2009; Smee & Sidwell, 2003; Beraldo & Gambino, 2004) as well as for their metal chelating properties (Paterson & Donnelly, 2011; Casas *et al.*, 2000). The molecular structure of the title compound (**I**) with numbering scheme is shown in Fig. 1. Recently, two crystal forms of 4-phenyl-1-(propan-2-ylidene)thiosemicarbazone have been reported. However, they were not identified as polymorphs (Jian *et al.*, 2005, CSD *Refcode*: FIDDUS; Venkatraman *et al.*, 2005, *Refcode*: FIDDUS01). Crystals of FIDDUS were obtained by recrystallisation from dimethyl sulfoxide, while those of FIDDUS01 from an acetone:methanol solution. The crystal structure reported here is similar to the lower density polymorph, FIDDUS ($d = 1.258 \text{ Mg/m}^3$ vs. 1.302 Mg/m^3 for FIDDUS01).

The bond lengths confirm the thione form of the title molecule, the presence of a double bond between the N3 and C2 atoms, and they indicate some π -delocalisation along the thiosemicarbazone fragment. The S1 and the hydrazinic N3 atoms are in the *trans* conformation with the S1—C1—N2—N3 torsion angle equal to $-177.7(3)^\circ$. This conformation enables the formation of an intramolecular N1—H \cdots N3 hydrogen bond. Consequently, the thiosemicarbazone part of the molecule (N1—C1—S1—N2—N3) is planar, with the maximum deviation from the mean plane of these atoms being $0.014(2) \text{ \AA}$ for N3. This conformation seems to be characteristic of the thiosemicarbazone fragment, and it is observed in all related crystal structures found in the CSD (Allen, 2002) [*Refcodes*: CUZXOK (Parsons *et al.*, 2000), DAWPOG (Park & Ahn, 1985), FIDDUS (Jian *et al.*, 2005), FIDDUS01 (Venkatraman *et al.*, 2005) and UQOWAZ (Basu & Das, 2011)]. The dihedral angles between the central thiosemicarbazone plane of (**I**) and the planes formed by the propan-2-ylidene (C2—C3—C4) and phenyl (C1P to C6P) groups are $16.7(4)$ and $38.9(2)^\circ$, respectively. For comparison, the respective angles in FIDDUS are 14.0° and 38.6° ; and in FIDDUS01 they are 23.6° and 42.8° .

The thiosemicarbazone part is also involved in intermolecular (N2—H \cdots S1) hydrogen bonds (Fig. 2, Table 1), resulting in $R^2_2(8)$ centrosymmetric dimers. (The same pattern have been found in DAWPOG, FIDDUS, FIDDUS01 and UQOWAZ.) The main difference between the two aforementioned polymorphs is the orientation of the molecules relative to the twofold screw axes. In FIDDUS and in (**I**) the 2_1 screw axis passes through the C1—N1 bond, while in FIDDUS01 it runs through the N2—N3 bond (Figs. 3 and 4). Additionally, in FIDDUS01 the thiosemicarbazone plane is almost perpendicular to the *b* direction (85.7°) while in FIDDUS and in (**I**) the corresponding angles are 62.0° and $59.9(4)^\circ$, respectively. In (**I**) and in FIDDUS there are offset stacking interactions between the aromatic rings (Fig. 3) with interplanar distances of $3.5(1) \text{ \AA}$ and 3.6 \AA , respectively. The physical consequence of these stacking interactions is the yellow colour of FIDDUS crystals, in contrast to the colourless crystals of FIDDUS01, where overlapping of the heteroatoms is observed (Fig. 4). Surprisingly, the crystals of (**I**) are colourless, despite the similar molecular and crystal structure with FIDDUS. This could be explained by the changes in the electronic structure of the aromatic ring in molecule (**I**) caused by the electronegative fluorine substituent. The presence of the fluorine atom in (**I**) causes only slight differences in crystal packing with respect to FIDDUS. In (**I**) there is a short intermolecular contact between the F1 and

C2 ($1 - x, 1/2 + y, 0.5 - z$) atoms with a distance of 3.107 (5) Å (the sum of van der Waals radii is 3.17 Å).

S2. Experimental

The title compound, $C_{10}H_{12}FN_3S$, was obtained in the reaction of 4-amino-1,7,8,9,10-pentamethyl-4-azatricyclo[2.5.1.0^{2,6}]dec-8-ene-3,5-dione and 3-fluorophenyl isothiocyanate in acetonitrile. The mixture of the reagents was refluxed for 6 h. After heating, the solvent was removed on a rotary evaporator. The residue was purified by column chromatography (chloroform:methanol 5.5:0.5). Two products were obtained in this reaction, *viz.*: 1-(3-fluorophenyl)-3-(1,7,8,9,10-pentamethyl-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)thiourea (60%) and 4-(3-fluorophenyl)-1-(propan-2-ylidene)thiosemicarbazone (40%). The title compound was recrystallised from acetonitrile.

S3. Refinement

All C-bonded H atoms were positioned geometrically and allowed to ride on the attached atom with C—H bond lengths of 0.93 Å for aromatic atoms and 0.96 Å for methyl groups. The positions of N-bonded H atoms were located in the difference electron density maps and then constrained with an N—H distance of 0.86 Å. $U_{iso}(H)$ values were fixed to $1.2U_{eq}(C,N)$.

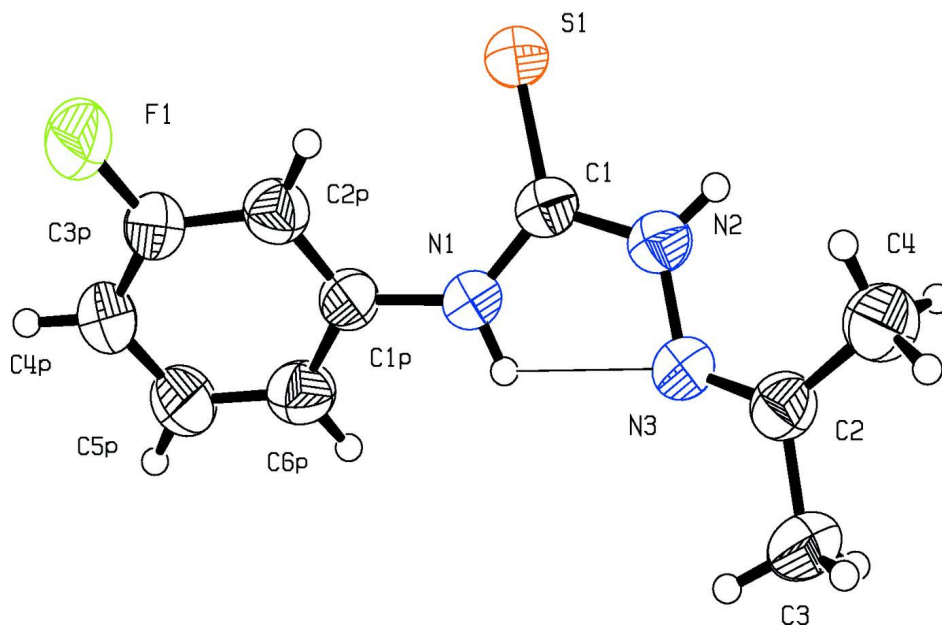
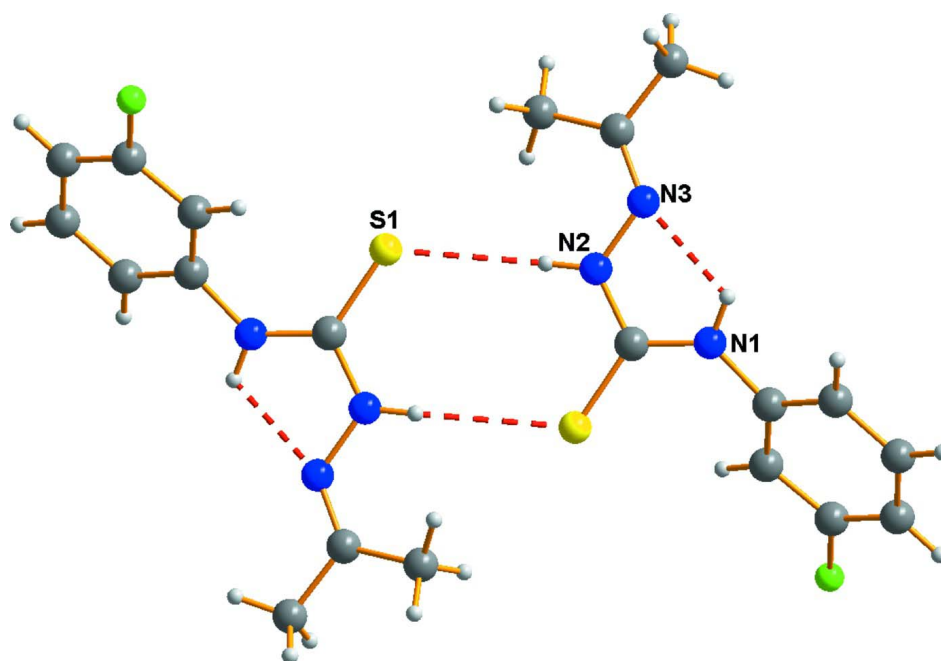
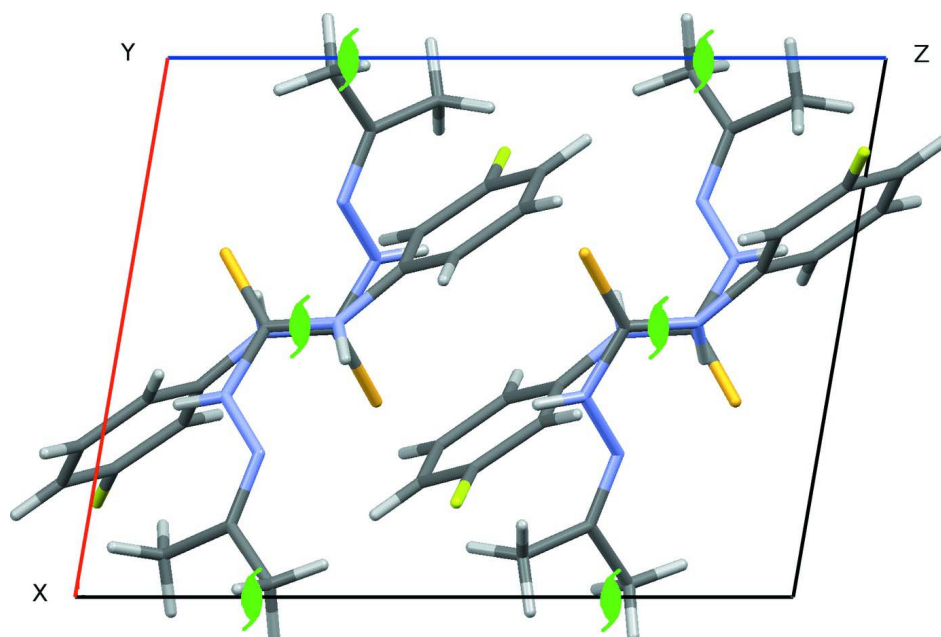


Figure 1

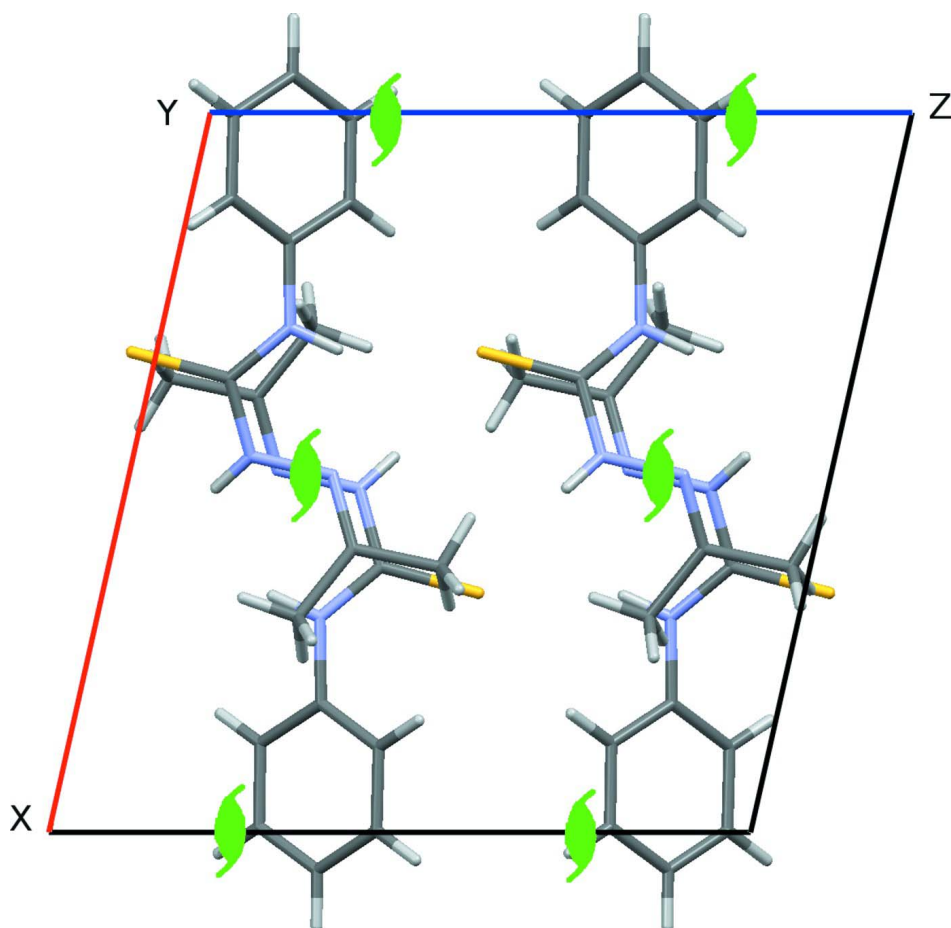
Molecular structure of the title compound with 50% probability displacement ellipsoids. H atoms are shown as small spheres of an arbitrary size. Thin single line represents the intramolecular hydrogen bond.

**Figure 2**

Dimer in (I) formed by hydrogen bonds around a centre of symmetry.

**Figure 3**

Orientation of molecules in relation to the 2_1 screw axes in (I). View along the b axis. Green symbols indicate the positions of 2_1 screw axes in the unit cells.

**Figure 4**

Orientation of molecules in relation to the 2_1 screw axes in FIDDUS01. View along b axis. Green symbols indicate positions of 2_1 screw axes in the unit cells.

***N*-(3-fluorophenyl)-2-(propan-2-ylidene)hydrazinecarbothioamide**

Crystal data

$C_{10}H_{12}FN_3S$

$M_r = 225.29$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 9.038\ (2)\ \text{\AA}$

$b = 10.515\ (2)\ \text{\AA}$

$c = 11.869\ (2)\ \text{\AA}$

$\beta = 99.77\ (3)^\circ$

$V = 1111.6\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 472$

$D_x = 1.346\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54178\ \text{\AA}$

Cell parameters from 75 reflections

$\theta = 6\text{--}20^\circ$

$\mu = 2.48\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Plate, colourless

$0.55 \times 0.30 \times 0.10\ \text{mm}$

Data collection

Kuma KM-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω - 2θ scans

Absorption correction: for a cylinder mounted
on the φ axis

(Dwiggins, 1975)

$T_{\min} = 0.435$, $T_{\max} = 0.485$

3800 measured reflections

1942 independent reflections
 1252 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.084$
 $\theta_{\text{max}} = 67.7^\circ$, $\theta_{\text{min}} = 5.0^\circ$
 $h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$
 $l = 0 \rightarrow 14$
 3 standard reflections every 100 reflections
 intensity decay: 3.3%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.217$
 $S = 1.04$
 1942 reflections
 138 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
 $w = 1/[\sigma^2(F_o^2) + (0.1522P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.013$
 $\Delta\rho_{\text{max}} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. cylinder dimensions used for absorption correction: 0.2 mm radius and a 0.1 mm height

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4980 (4)	0.4433 (3)	0.2021 (3)	0.0493 (8)
C1P	0.3908 (4)	0.4006 (4)	0.3776 (3)	0.0506 (9)
C2	0.8673 (4)	0.3455 (4)	0.1991 (3)	0.0557 (9)
C2P	0.3249 (5)	0.5171 (4)	0.3911 (3)	0.0566 (9)
H2P	0.3381	0.5864	0.3451	0.068*
C3	0.9760 (5)	0.2575 (6)	0.2680 (4)	0.0785 (14)
H3A	0.9395	0.2344	0.3366	0.094*
H3B	1.0715	0.2989	0.2876	0.094*
H3C	0.9870	0.1823	0.2242	0.094*
C3P	0.2380 (5)	0.5252 (4)	0.4767 (4)	0.0613 (10)
C4	0.9221 (5)	0.4267 (5)	0.1128 (4)	0.0718 (13)
H4A	0.9086	0.3830	0.0408	0.086*
H4B	1.0268	0.4448	0.1373	0.086*
H5C	0.8665	0.5049	0.1046	0.086*
C4P	0.2123 (5)	0.4283 (5)	0.5460 (4)	0.0675 (11)
H4P	0.1521	0.4384	0.6015	0.081*
C5P	0.2802 (6)	0.3136 (5)	0.5299 (4)	0.0700 (12)
H5P	0.2662	0.2447	0.5761	0.084*
C6P	0.3682 (5)	0.2991 (4)	0.4467 (4)	0.0639 (11)

H6P	0.4124	0.2209	0.4370	0.077*
N1	0.4913 (4)	0.3838 (3)	0.3000 (3)	0.0564 (8)
H1	0.5586	0.3263	0.3189	0.068*
N2	0.6276 (4)	0.4233 (3)	0.1607 (3)	0.0560 (8)
H2	0.6427	0.4587	0.0983	0.067*
N3	0.7337 (4)	0.3444 (4)	0.2220 (3)	0.0567 (8)
S1	0.36293 (11)	0.53442 (10)	0.12753 (8)	0.0578 (4)
F1	0.1751 (4)	0.6403 (3)	0.4920 (3)	0.0941 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0477 (18)	0.0465 (19)	0.0519 (19)	0.0021 (16)	0.0037 (14)	-0.0012 (15)
C1P	0.0412 (17)	0.061 (2)	0.0499 (18)	0.0004 (16)	0.0070 (14)	0.0020 (16)
C2	0.052 (2)	0.057 (2)	0.058 (2)	0.0001 (18)	0.0065 (17)	-0.0026 (18)
C2P	0.063 (2)	0.052 (2)	0.055 (2)	0.0007 (18)	0.0113 (17)	0.0036 (17)
C3	0.062 (3)	0.099 (3)	0.073 (3)	0.027 (3)	0.006 (2)	0.007 (3)
C3P	0.072 (3)	0.061 (2)	0.0521 (19)	0.012 (2)	0.0145 (18)	-0.0026 (18)
C4	0.049 (2)	0.087 (3)	0.078 (3)	-0.008 (2)	0.0078 (19)	0.011 (3)
C4P	0.071 (3)	0.078 (3)	0.058 (2)	0.008 (2)	0.0247 (19)	0.007 (2)
C5P	0.075 (3)	0.071 (3)	0.068 (3)	0.001 (2)	0.026 (2)	0.016 (2)
C6P	0.068 (3)	0.057 (2)	0.067 (2)	0.006 (2)	0.0116 (19)	0.0073 (19)
N1	0.0545 (18)	0.0620 (19)	0.0541 (17)	0.0156 (16)	0.0133 (13)	0.0080 (15)
N2	0.0498 (17)	0.0609 (18)	0.0572 (18)	0.0055 (15)	0.0087 (13)	0.0070 (15)
N3	0.0502 (17)	0.064 (2)	0.0564 (17)	0.0092 (15)	0.0107 (14)	0.0049 (15)
S1	0.0535 (6)	0.0664 (7)	0.0528 (6)	0.0100 (5)	0.0069 (4)	0.0064 (4)
F1	0.139 (3)	0.0729 (18)	0.0802 (18)	0.0358 (19)	0.0475 (18)	0.0055 (15)

Geometric parameters (Å, °)

C1—N1	1.331 (5)	C3P—C4P	1.354 (6)
C1—N2	1.361 (5)	C3P—F1	1.362 (5)
C1—S1	1.681 (4)	C4—H4A	0.9600
C1P—C6P	1.382 (6)	C4—H4B	0.9600
C1P—C2P	1.383 (6)	C4—H5C	0.9600
C1P—N1	1.409 (5)	C4P—C5P	1.381 (7)
C2—N3	1.282 (5)	C4P—H4P	0.9300
C2—C4	1.482 (6)	C5P—C6P	1.377 (6)
C2—C3	1.489 (6)	C5P—H5P	0.9300
C2P—C3P	1.389 (6)	C6P—H6P	0.9300
C2P—H2P	0.9300	N1—H1	0.8600
C3—H3A	0.9600	N2—N3	1.379 (5)
C3—H3B	0.9600	N2—H2	0.8600
C3—H3C	0.9600		
N1—C1—N2	114.4 (3)	C2—C4—H4B	109.5
N1—C1—S1	126.2 (3)	H4A—C4—H4B	109.5
N2—C1—S1	119.4 (3)	C2—C4—H5C	109.5

C6P—C1P—C2P	120.3 (4)	H4A—C4—H5C	109.5
C6P—C1P—N1	117.9 (4)	H4B—C4—H5C	109.5
C2P—C1P—N1	121.6 (4)	C3P—C4P—C5P	116.6 (4)
N3—C2—C4	126.1 (4)	C3P—C4P—H4P	121.7
N3—C2—C3	115.8 (4)	C5P—C4P—H4P	121.7
C4—C2—C3	118.1 (4)	C6P—C5P—C4P	121.3 (4)
C1P—C2P—C3P	116.6 (4)	C6P—C5P—H5P	119.3
C1P—C2P—H2P	121.7	C4P—C5P—H5P	119.3
C3P—C2P—H2P	121.7	C5P—C6P—C1P	120.1 (4)
C2—C3—H3A	109.5	C5P—C6P—H6P	119.9
C2—C3—H3B	109.5	C1P—C6P—H6P	119.9
H3A—C3—H3B	109.5	C1—N1—C1P	129.9 (3)
C2—C3—H3C	109.5	C1—N1—H1	115.0
H3A—C3—H3C	109.5	C1P—N1—H1	115.0
H3B—C3—H3C	109.5	C1—N2—N3	117.8 (3)
C4P—C3P—F1	118.1 (4)	C1—N2—H2	121.1
C4P—C3P—C2P	125.0 (4)	N3—N2—H2	121.1
F1—C3P—C2P	116.9 (4)	C2—N3—N2	118.6 (4)
C2—C4—H4A	109.5		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...N3	0.86	2.12	2.553 (5)	111
N2—H2...S1 ⁱ	0.86	2.67	3.465 (3)	154

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