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Crystal structure and Hirshfeld surface analysis of ethyl (3*E*)-5-(4-fluorophenyl)3-{[(4-methoxyphenyl)formamido]imino}-7-methyl-2*H*,3*H*,5*H*-[1,3]-thiazolo[3,2-*a*]pyrimidine-6-carboxylate 0.25-hydrate

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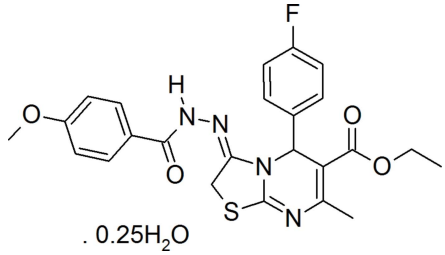
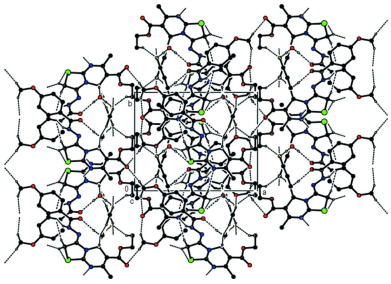
In the title compound, $C_{24}H_{23}FN_4O_4S\cdot0.25H_2O$, the dihydropyrimidine ring is distinctly non-planar, with the flap C atom deviating by 0.297 (2) Å from the least-squares plane. In the crystal, zigzag chains are formed by N—H···N hydrogen bonds parallel to [010] and are connected into layers parallel to (100) by O—H···O, O—H···F, C—H···O, C—H···F and C—H···N hydrogen bonds. Additional C—H···O hydrogen bonds connect the layers into a three-dimensional network. A Hirshfeld surface analysis indicates that the most significant contributions to the crystal packing are from H···H (42.6%), O···H/H···O (16.8%) and C···H/H···C (15.5%) contacts.

1. Chemical context

Interest in the anticancer activities of dihydropyrimidines (DHPMs) has been increasing since 1999, when monastrol was discovered (Mayer *et al.*, 1999; Leizerman *et al.*, 2004). In addition, 1,3,4-oxadiazole has been reported to exhibit a significant anticancer activity (Yadagiri *et al.*, 2015; Valente *et al.*, 2014; El-Din *et al.*, 2015). Since the combination of two or more pharmacophoric structural moieties can possibly augment the bioactivity, it was of interest to hybridize the DHPM moiety with 1,3,4-oxadiazole, hoping to discover potent anticancer agents.



In this context, a target compound was designed through the condensation of 6-methyl-4-aryl-1,2,3,4-tetrahydropyrimidine-2(1*H*)-thione derivatives and 2-(chloromethyl)-5-aryl-1,3,4-oxadiazole derivatives (Ragab *et al.*, 2017). Unexpectedly, an intramolecular cyclization and ring opening of 1,3,4-



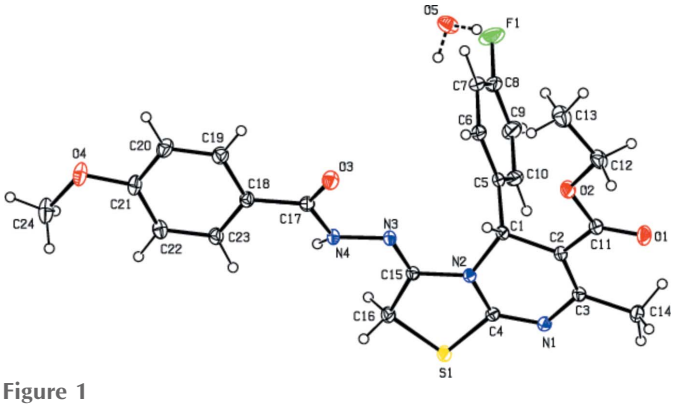


Figure 1
The title molecule with the labelling scheme and displacement ellipsoids drawn at the 30% probability level.

oxadiazole occurred. The resulting product was chosen as an example of this series for further structural elucidation through X-ray crystallography. Herein we report the crystal structure and Hirshfeld analysis of the title compound, $C_{24}H_{23}FN_4O_4S{\cdot}0.25H_2O$.

2. Structural commentary

In the title compound (Fig. 1), the dihydropyrimidine portion (N1/C3/C2/C1/N2/C4) of the central ring is planar to within 0.0286 (9) Å (r.m.s. deviation of the fitted atoms = 0.0211 Å), with the flap C1 atom being 0.297 (2) Å out of this plane towards the bonded 4-fluorophenyl group. A puckering analysis (Cremer & Pople, 1975) of this ring yielded the parameters Q = 0.2074 (15) Å, θ = 112.1 (4)° and φ = 3.5 (4)°. The dihedral angle between the C5–C10 phenyl ring and the least-squares plane of the dihydropyrimidine plane is 88.76 (5)°. The C4/N2/C15/C16/S1 ring is planar to within 0.0191 (8) Å (r.m.s. deviation of the fitted atoms = 0.0140 Å) and is inclined to the N1/C3/C2/C1/N2/C4 plane by 3.99 (9)°. The dihedral angle between the C4/N2/C15/C16/S1 ring and the C18–C23 phenyl ring is 9.28 (8)°.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N1^{i}	0.885 (19)	2.164 (19)	2.9888 (17)	154.8 (16)
C1—H1···O5^{ii}	0.987 (17)	2.345 (18)	3.307 (5)	164.7 (13)
C7—H7···O4^{iii}	0.97 (2)	2.41 (2)	3.285 (2)	148.7 (17)
C13—H13B···F1^{ii}	0.98 (3)	2.49 (3)	3.386 (2)	153.0 (19)
C16—H16A···N1^{i}	0.98 (2)	2.58 (2)	3.4019 (19)	142.4 (15)
C16—H16B···O5^{iv}	0.98 (2)	2.37 (2)	3.282 (5)	154.6 (16)
C24—H24A···O1^{v}	0.99 (2)	2.53 (2)	3.450 (3)	154.6 (18)
C24—H24C···O1^{vi}	0.95 (2)	2.57 (2)	3.504 (2)	167.8 (17)
O5—H5A···F1	0.87	1.76	2.479 (5)	138
O5—H5B···O3^{vii}	0.87	2.00	2.863 (5)	174

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

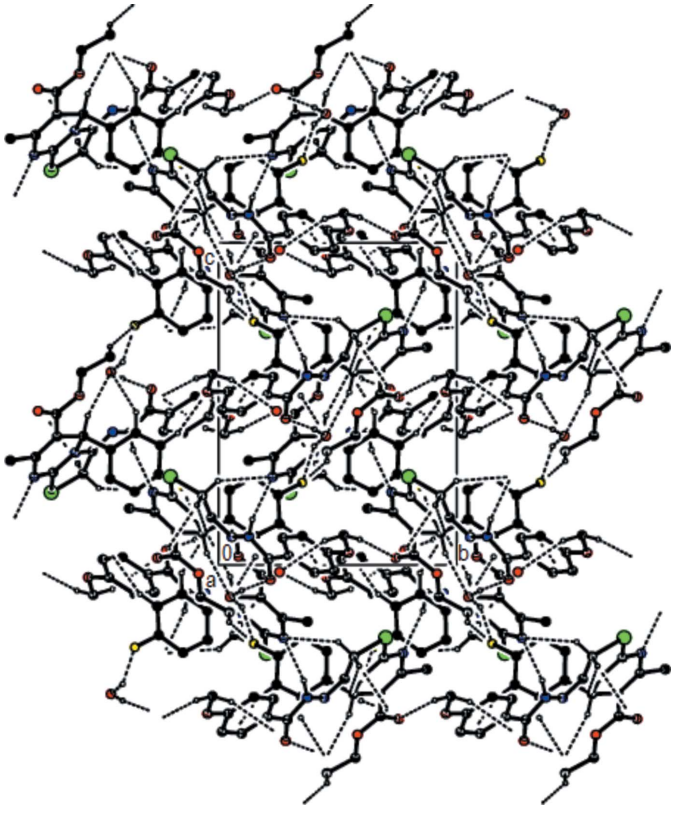


Figure 2
View of the molecular packing along [100]. O—H···O, O—H···F, C—H··· O, C—H···N and C—H···F hydrogen bonds are shown as dashed lines.

3. Supramolecular features

In the crystal, molecules are connected into zigzag chains running parallel to [010] by N4—H4···N1 hydrogen bonds (Table 1). The chains are connected into (100) layers by O5—

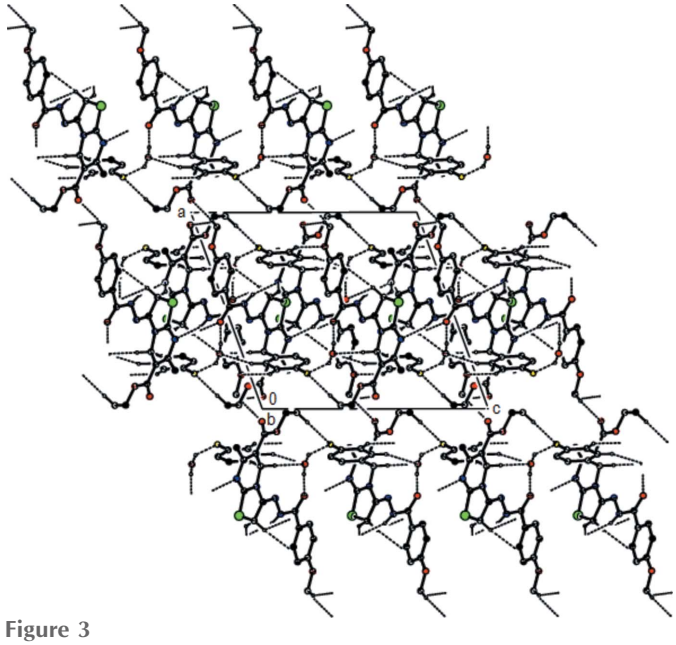


Figure 3
View of the molecular packing along [010]. Hydrogen bonds are depicted as in Fig. 2.

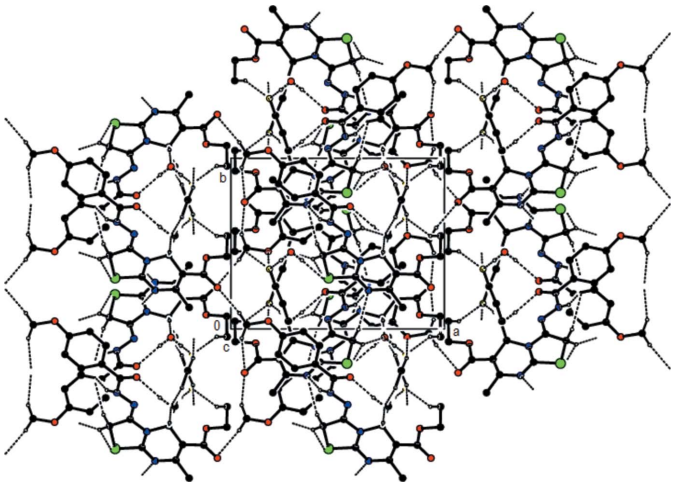


Figure 4
View of the molecular packing along [001]. Hydrogen bonds are depicted as in Fig. 2.

H5*B*···O3 and O5—H5*A*···F1 hydrogen bonds involving the water molecule, as well as by C13—H13*B*···F1, C16—H16*A*···N1 and all of the C—H···O hydrogen bonds listed in Table 1, except for the C24—H24*C*···O1 hydrogen bond (Figs. 2, 3 and 4) that serves to link the layers into a three-dimensional network.

4. Hirshfeld surface analysis

A Hirshfeld surface analysis was performed, and two-dimensional fingerprint plots were constructed using *Crystal Explorer17.5* to quantify the intermolecular interactions in the title molecule (Turner *et al.*, 2017). Fig. 5 depicts the Hirshfeld surface plotted over d_{norm} in the range −0.7253 to +1.4745 arbitrary units, with red patches indicating putative hydrogen bonding in the crystal structure.

The intensity of the red patches is more pronounced for N4—H4···N1, C1—H1···O5, C16—H16*B*···O5, C24—H24*A*···O1, C24—H24*C*···O1 and O5—H5*B*···O3, thus revealing the strongest interactions when compared to other red spots on the Hirshfeld surface. Table 2 gives numerical data for close intermolecular contacts. The two-dimensional fingerprint plots (Fig. 6) shows that the largest contributions are from H···H (42.6%; Fig. 6*b*), O···H/H···O (16.8%; Fig. 6*c*) and C···H/H···C (15.5%; Fig. 6*d*) interactions. Other interactions contributing less to the crystal packing are from F···H/H···F (6.7%), N···H/H···N (4.5%), S···H/H···S (3.4%), S···C/C···S (3.4%), C···C (2.8%), S···N/N···S (1.4%),N···C/C···N (1.4%), O···C/C···O (0.7%), N···N (0.5%), O···N/N···O (0.2%) and S···O/O···S (0.1%) interactions.

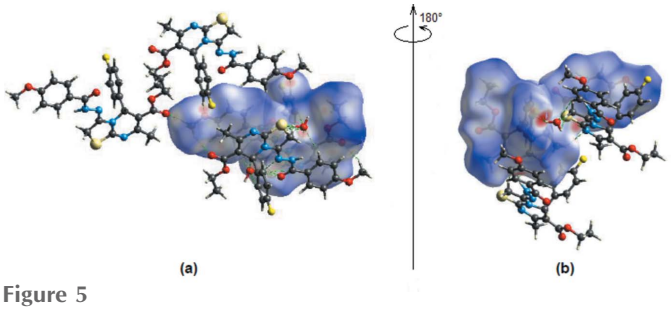


Figure 5
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm}, with a fixed colour scale of −0.7253 (red) to +1.4745 (blue) a.u.

Table 2
Summary of short interatomic contacts (Å) in the title compound..

Asterisks relate to atoms of the underoccupied water molecule.

Contact	Distance	Symmetry operation
N1···H4	2.165	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
F1···H13*B*	2.49	$x, \frac{3}{2}-y, -\frac{1}{2}+z$
F1···*H5*A*	1.76	x, y, z
F1···H14*C*	2.66	$x, 1+y, z$
H14*A*···H24*C*	2.56	$1+x, -1+y, z$
H12*C*···O1	2.66	$2-x, 1-y, 1-z$
H16*B*···O3	2.49	$1-x, 1-y, 1-z$
O3···*H5*B*	2.00	$x, \frac{3}{2}-y, \frac{1}{2}+z$
H7···O4	2.41	$1-x, 2-y, 1-z$
H16*B*···*H5*B*	2.05	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
H13*A*···H24*B*	2.41	$1+x, \frac{3}{2}-y, \frac{1}{2}+z$
H14*C*···*O5	2.87	$x, -1+y, z$

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016)

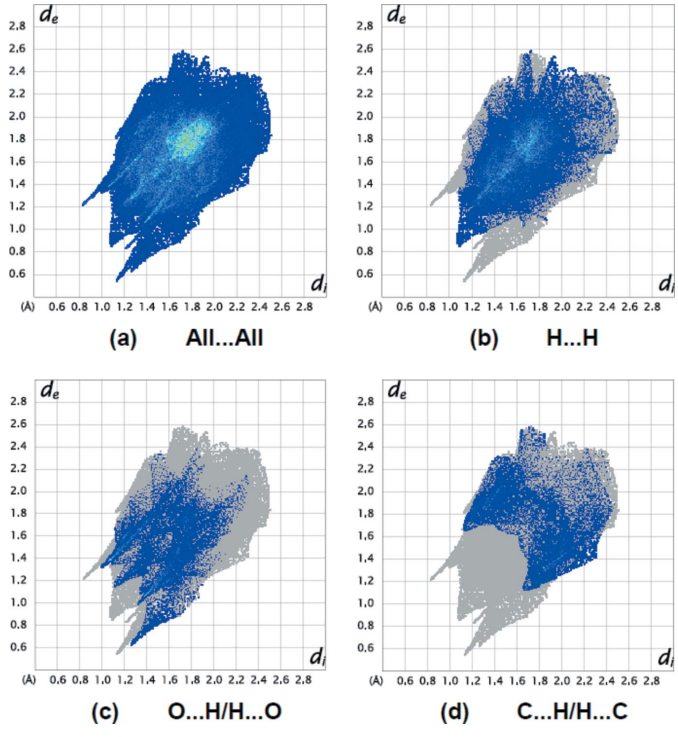


Figure 6
Two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) O···H/H···O and (*d*) C···H/H···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

for compounds most closely related to the 2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyrimidine unit of the title compound gave the following hits: refcodes ZOWXAM (**I**) (Krishnamurthy *et al.*, 2014); PONVOF (**II**) (Krishnamurthy & Begum, 2014); AFIZUM (**III**) (Fathima *et al.*, 2013); YAYHAJ (**IV**) (Nagarajaiah *et al.*, 2012); KUSQUL (**V**) (Jotani *et al.*, 2010*a*); PUJRIW (**VI**) (Jotani *et al.*, 2010*b*); DIWSIM (**VII**) (Jotani & Baldaniya, 2008); TICHAP (**VIII**) (Jotani & Baldaniya, 2007); AWUPAK (**IX**) (Fun *et al.*, 2011); XETKOX (**X**) (Sridhar *et al.*, 2006) and XETKOX01 (**XI**) (Sridhar *et al.*, 2006).

In the crystal of (**I**), pairs of weak C—H···O hydrogen bonds link molecules related by twofold rotation axes, forming $R_2^2(10)$ rings, which in turn are linked by weak C—H···N interactions to form chains parallel to [010]. In addition, weak C—H···π(arene) interactions link the chains into layers parallel to (001), and π–π interactions connect these layers into a three-dimensional network.

In (**II**), weak C—H···F and C— H···O hydrogen bonds connect molecules, forming zigzag chains parallel to [010]. In addition, π–π stacking interactions connect these chains into ladders *via* inversion-related 4-fluorophenyl groups.

In (**III**), pairs of weak C—H···O hydrogen bonds lead to the formation of inversion dimers. A weak C—H···π interaction and π–π stacking interactions are observed.

In (**IV**), O—H···N and C— H···S interactions result in (001) layers. The supramolecular assembly is stabilized by π–π stacking interactions between the 2-bromobenzylidene and thiazolopyrimidine rings. In addition, C—H···π interactions are also observed.

In (**V**), co-operative C—H···O and C—H···π interactions lead to supramolecular chains parallel [100]. These chains are connected *via* π–π interactions.

The crystal packing of (**VI**) is influenced by weak intermolecular C—H···π interactions and π–π stacking between the thiazole and phenyl rings, which stack the molecules parallel to [001].

In (**VII**), in addition to intermolecular C— H···O hydrogen bonding, short intramolecular C—H···S contacts and π–π stacking interactions contribute to the crystal packing.

In (**VIII**), short intermolecular C—H···O, C—H···π and π–π stacking interactions contribute to the stability of the crystal packing.

In (**IX**), molecules are linked into a three-dimensional network by intermolecular C— H···O and C—H···F hydrogen bonds. The crystal structure is further stabilized by a C—H···π interaction.

Compounds (**X**) and (**XI**) crystallize in two polymorphic forms having the same space-group type, *viz*. *P*1, with $Z' = 2$ and $Z' = 1$. In both polymorphs, the molecules are linked by N—H···O and C—H···O hydrogen bonds.

6. Synthesis and crystallization

A mixture of ethyl 4-(4-fluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2 mmol), 2-(chloromethyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (2 mmol), potassium iodide (2 mmol) and triethyl amine (2.5 mmol), was refluxed for 4 h in absolute ethanol (20 ml). The reaction mixture was poured onto crushed ice (40 g) and acidified with acetic acid (2 ml). The deposited precipitate was filtered off, washed with cold water, dried and recrystallized from a methanol/DMF mixture.

Yield: 95%; melting point: 493–495 K; IR (KBr) ν_{max}/cm^{-1} 3390, 3178, 1693, 1654. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.60 (*s*, 1H, NH), 7.81 (*d*, *J* = 8.7 Hz, 2H, Ar—H), 7.44 (*t*, *J* = 7.7 Hz, 2H, Ar—H), 7.15 (*t*, *J* = 7.7 Hz, 2H, Ar—H), 7.03 (*d*, *J* = 8.7 Hz, 2H, Ar—H), 6.13 (*s*, 1H, C4—H), 4.45 (*d*, *J* = 17.4 Hz, 1H, S—CH$_2$), 4.35 (*d*, *J* = 17.3 Hz, 1H, S—CH$_2$), 4.03 (*q*, *J* = 7.1 Hz, 2H, CH$_2$—CH$_3$), 3.82 (*s*, 3H, OCH$_3$), 2.34 (*s*, 3H, C6-CH$_3$), 1.11 (*t*, *J* = 7.1 Hz, 3H, CH$_2$—CH$_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.59, 163.23, 163.20, 162.65, 153.92, 153.58, 130.57, 130.50, 130.03, 125.90, 115.64, 115.47, 114.05, 105.95, 60.28, 55.87, 54.89, 28.56, 23.06, 14.45. Analysis calculated for $C_{24}H_{23}FN_4O_4S$ (482.53): C 59.74, H 4.80, N 11.61. Found: C 60.02, H 4.89, N 11.87.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{23}FN_4O_4S{\cdot}0.25H_2O$
M_r	487.03
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	14.4316 (3), 10.8518 (2), 15.5940 (3)
β (°)	109.941 (1)
V (Å^3)	2295.74 (8)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.68
Crystal size (mm)	0.15 × 0.14 × 0.11
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.75, 0.84
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17597, 4576, 4142
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.088, 1.04
No. of reflections	4576
No. of parameters	409
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.56

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *publCIF* (Westrip, 2010).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were found in difference-Fourier maps; all C and N-bound H atoms were refined freely. The water molecule was found to be occupationally disordered and was refined with a fixed site occupa-

tion factor of 1/4. The H atoms of the water molecules were located in a difference-Fourier map, their bond lengths set to an ideal value of 0.87 Å, and were refined with U_{iso}(H) = 1.5 U_{eq}(O) using a riding model.

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Author contributions are as follows: synthesis and organic chemistry parts preparation, AMA, FAFR, SKM; conceptualization and study guide, AMA, SKM; financial support, MAA **MAU?**; crystal data production and validation, JTM; paper preparation and Hirshfeld study, MA, SKM.

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supporting information

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Crystal structure and Hirshfeld surface analysis of ethyl (3*E*)-5-(4-fluorophenyl)3-{[(4-methoxyphenyl)formamido]imino}-7-methyl-2*H*,3*H*,5*H*-[1,3]thiazolo[3,2-*a*]pyrimidine-6-carboxylate 0.25-hydrate

Shaaban K. Mohamed, Joel T. Mague, Mehmet Akkurt, Abdallah M. Alfayomy, Fatma A. F. Ragab and Mokhtar A. Abd ul-Malik

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Ethyl (3*E*)-5-(4-fluorophenyl)3-{[(4-methoxyphenyl)formamido]imino}-7-methyl-2*H*,3*H*,5*H*-[1,3]thiazolo[3,2-*a*]pyrimidine-6-carboxylate 0.25-hydrate

Crystal data

$C_{24}H_{23}FN_4O_4S·0.25H_2O$
M_r = 487.03
Monoclinic, $P2_1/c$
a = 14.4316 (3) Å
b = 10.8518 (2) Å
c = 15.5940 (3) Å
β = 109.941 (1)°
V = 2295.74 (8) Å^3
Z = 4
$F(000)$ = 1018
D_x = 1.409 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9970 reflections
θ = 3.3–74.4°
μ = 1.68 mm^{-1}
T = 150 K
Block, colourless
0.15 × 0.14 × 0.11 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.75, T_{max} = 0.84
17597 measured reflections
4576 independent reflections
4142 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 74.4°, θ_{min} = 3.3°
h = −17→18
k = −13→12
l = −19→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 1.04
4576 reflections
409 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 1.1637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL-2018/1* (Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00229 (19)

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. Refinement of the site occupancy factor for the lattice water (O5) converged at *ca.* 0.25. This was fixed at this value for the remainder of the refinement, the attached hydrogen atoms were located in a difference map and included as riding contributions in idealized positions.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.45709 (2)	0.29846 (3)	0.22568 (2)	0.02637 (11)	
F1	0.81951 (11)	0.85095 (10)	0.24433 (11)	0.0709 (4)	
O1	0.93592 (8)	0.24379 (11)	0.47803 (8)	0.0365 (3)	
O2	0.88439 (7)	0.41670 (10)	0.52684 (7)	0.0294 (2)	
O3	0.55706 (8)	0.71812 (10)	0.54550 (7)	0.0307 (2)	
O4	0.17420 (9)	1.04606 (11)	0.46165 (8)	0.0390 (3)	
N1	0.64445 (8)	0.22708 (11)	0.27415 (8)	0.0220 (2)	
N2	0.60560 (8)	0.39869 (10)	0.34918 (8)	0.0200 (2)	
N3	0.54560 (8)	0.55654 (10)	0.41266 (8)	0.0206 (2)	
N4	0.46512 (8)	0.62737 (11)	0.41154 (8)	0.0209 (2)	
H4	0.4182 (14)	0.6419 (17)	0.3587 (13)	0.032 (5)*	
C1	0.70873 (9)	0.43284 (13)	0.40035 (10)	0.0213 (3)	
H1	0.7122 (12)	0.4512 (15)	0.4634 (11)	0.022 (4)*	
C2	0.77324 (10)	0.32264 (13)	0.39918 (10)	0.0224 (3)	
C3	0.74171 (10)	0.23233 (13)	0.33574 (10)	0.0224 (3)	
C4	0.58287 (10)	0.30597 (12)	0.28731 (9)	0.0207 (3)	
C5	0.73684 (9)	0.54708 (13)	0.35807 (10)	0.0233 (3)	
C6	0.76870 (10)	0.65331 (14)	0.40974 (11)	0.0291 (3)	
H6	0.7696 (14)	0.6545 (17)	0.4744 (13)	0.035 (5)*	
C7	0.79756 (12)	0.75620 (15)	0.37183 (14)	0.0365 (4)	
H7	0.8223 (15)	0.829 (2)	0.4092 (14)	0.048 (6)*	
C8	0.79149 (13)	0.75033 (15)	0.28209 (14)	0.0410 (4)	
C9	0.75793 (15)	0.64862 (16)	0.22793 (14)	0.0420 (4)	
H9	0.7526 (16)	0.651 (2)	0.1629 (15)	0.050 (6)*	

C10	0.73134 (12)	0.54590 (14)	0.26730 (11)	0.0314 (3)	
H10	0.7067 (14)	0.4745 (19)	0.2304 (13)	0.038 (5)*	
C11	0.87186 (10)	0.32007 (13)	0.46924 (10)	0.0253 (3)	
C12	0.97996 (11)	0.42561 (17)	0.59855 (11)	0.0331 (3)	
H12A	0.9878 (15)	0.353 (2)	0.6404 (14)	0.045 (5)*	
H12B	1.0316 (14)	0.4216 (17)	0.5703 (12)	0.034 (5)*	
H12C	0.9642 (16)	0.618 (2)	0.6014 (15)	0.052 (6)*	
C13	0.98133 (13)	0.5454 (2)	0.64668 (13)	0.0412 (4)	
H13A	1.0491 (17)	0.557 (2)	0.6929 (15)	0.055 (6)*	
H13B	0.9329 (18)	0.545 (2)	0.6776 (16)	0.060 (7)*	
C14	0.80354 (11)	0.12659 (15)	0.32406 (12)	0.0287 (3)	
H14A	0.8649 (17)	0.155 (2)	0.3186 (15)	0.052 (6)*	
H14B	0.8240 (16)	0.074 (2)	0.3764 (16)	0.054 (6)*	
H14C	0.7663 (16)	0.079 (2)	0.2696 (15)	0.046 (5)*	
C15	0.52713 (9)	0.47098 (12)	0.35314 (9)	0.0202 (3)	
C16	0.43099 (10)	0.43208 (14)	0.28344 (10)	0.0260 (3)	
H16A	0.4032 (14)	0.4974 (19)	0.2389 (13)	0.040 (5)*	
H16B	0.3839 (15)	0.4099 (18)	0.3141 (14)	0.043 (5)*	
C17	0.48023 (10)	0.71162 (13)	0.48039 (9)	0.0223 (3)	
C18	0.39469 (10)	0.79431 (13)	0.47152 (9)	0.0230 (3)	
C19	0.41359 (12)	0.90278 (14)	0.52329 (10)	0.0289 (3)	
H19	0.4793 (15)	0.9188 (17)	0.5629 (13)	0.036 (5)*	
C20	0.33869 (12)	0.98472 (15)	0.51747 (11)	0.0331 (3)	
H20	0.3508 (16)	1.062 (2)	0.5510 (15)	0.053 (6)*	
C21	0.24267 (11)	0.95909 (15)	0.46124 (10)	0.0294 (3)	
C22	0.22193 (11)	0.85134 (15)	0.40997 (10)	0.0287 (3)	
H22	0.1533 (15)	0.8314 (18)	0.3709 (13)	0.037 (5)*	
C23	0.29829 (11)	0.76979 (14)	0.41584 (10)	0.0260 (3)	
H23	0.2829 (13)	0.6946 (17)	0.3814 (12)	0.031 (5)*	
C24	0.07367 (14)	1.0253 (2)	0.40748 (14)	0.0456 (5)	
H24A	0.0502 (16)	0.946 (2)	0.4247 (15)	0.054 (6)*	
H24B	0.0650 (16)	1.025 (2)	0.3411 (16)	0.053 (6)*	
H24C	0.0390 (16)	1.093 (2)	0.4203 (14)	0.048 (6)*	
O5	0.7191 (3)	0.9508 (5)	0.0994 (3)	0.0378 (10)	0.25
H5A	0.766259	0.901704	0.130626	0.057*	0.25
H5B	0.667996	0.902764	0.079072	0.057*	0.25

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01757 (17)	0.0260 (2)	0.0312 (2)	0.00125 (12)	0.00266 (13)	−0.00720 (13)
F1	0.1061 (11)	0.0263 (6)	0.1191 (11)	−0.0171 (6)	0.0888 (10)	−0.0055 (6)
O1	0.0214 (5)	0.0345 (6)	0.0476 (7)	0.0093 (4)	0.0038 (5)	−0.0055 (5)
O2	0.0177 (5)	0.0313 (6)	0.0326 (6)	0.0026 (4)	0.0002 (4)	−0.0057 (4)
O3	0.0271 (5)	0.0336 (6)	0.0274 (5)	0.0038 (4)	0.0040 (4)	−0.0039 (4)
O4	0.0370 (6)	0.0405 (7)	0.0400 (6)	0.0175 (5)	0.0137 (5)	−0.0051 (5)
N1	0.0198 (5)	0.0194 (6)	0.0257 (6)	0.0010 (4)	0.0064 (5)	−0.0013 (4)
N2	0.0151 (5)	0.0186 (6)	0.0246 (6)	0.0011 (4)	0.0046 (4)	−0.0013 (4)

N3	0.0174 (5)	0.0202 (6)	0.0246 (6)	0.0028 (4)	0.0078 (4)	0.0011 (4)
N4	0.0179 (5)	0.0216 (6)	0.0231 (6)	0.0044 (4)	0.0069 (5)	0.0005 (4)
C1	0.0151 (6)	0.0211 (7)	0.0256 (7)	0.0001 (5)	0.0042 (5)	−0.0028 (5)
C2	0.0169 (6)	0.0208 (7)	0.0284 (7)	0.0019 (5)	0.0062 (5)	0.0005 (5)
C3	0.0190 (6)	0.0205 (7)	0.0276 (7)	0.0016 (5)	0.0079 (5)	0.0023 (5)
C4	0.0206 (6)	0.0181 (7)	0.0230 (7)	−0.0001 (5)	0.0067 (5)	0.0005 (5)
C5	0.0146 (6)	0.0199 (7)	0.0348 (8)	0.0012 (5)	0.0077 (5)	−0.0021 (5)
C6	0.0207 (7)	0.0237 (8)	0.0399 (9)	0.0007 (5)	0.0066 (6)	−0.0057 (6)
C7	0.0270 (8)	0.0204 (8)	0.0640 (11)	−0.0040 (6)	0.0179 (8)	−0.0093 (7)
C8	0.0439 (9)	0.0204 (8)	0.0744 (13)	−0.0032 (7)	0.0406 (9)	0.0001 (8)
C9	0.0582 (11)	0.0270 (9)	0.0568 (11)	−0.0018 (7)	0.0402 (10)	−0.0014 (7)
C10	0.0373 (8)	0.0227 (8)	0.0403 (9)	−0.0035 (6)	0.0212 (7)	−0.0051 (6)
C11	0.0191 (6)	0.0238 (7)	0.0312 (7)	0.0015 (5)	0.0064 (6)	−0.0005 (6)
C12	0.0177 (7)	0.0431 (10)	0.0315 (8)	0.0004 (6)	−0.0005 (6)	−0.0031 (7)
C13	0.0284 (8)	0.0560 (12)	0.0348 (9)	−0.0025 (8)	0.0053 (7)	−0.0140 (8)
C14	0.0239 (7)	0.0252 (8)	0.0356 (8)	0.0050 (6)	0.0083 (6)	−0.0037 (6)
C15	0.0171 (6)	0.0186 (7)	0.0246 (7)	0.0011 (5)	0.0068 (5)	0.0028 (5)
C16	0.0187 (6)	0.0254 (8)	0.0303 (8)	0.0020 (5)	0.0038 (6)	−0.0048 (6)
C17	0.0226 (7)	0.0217 (7)	0.0234 (7)	0.0007 (5)	0.0090 (5)	0.0015 (5)
C18	0.0246 (7)	0.0235 (7)	0.0234 (7)	0.0023 (5)	0.0113 (6)	0.0002 (5)
C19	0.0287 (8)	0.0288 (8)	0.0292 (8)	0.0003 (6)	0.0098 (6)	−0.0039 (6)
C20	0.0378 (9)	0.0286 (8)	0.0336 (8)	0.0043 (6)	0.0134 (7)	−0.0072 (6)
C21	0.0322 (8)	0.0313 (8)	0.0286 (8)	0.0110 (6)	0.0155 (6)	0.0018 (6)
C22	0.0254 (7)	0.0341 (8)	0.0283 (7)	0.0042 (6)	0.0114 (6)	−0.0016 (6)
C23	0.0256 (7)	0.0274 (8)	0.0273 (7)	0.0014 (6)	0.0121 (6)	−0.0035 (6)
C24	0.0357 (9)	0.0540 (12)	0.0455 (11)	0.0212 (9)	0.0119 (8)	−0.0026 (9)
O5	0.027 (2)	0.042 (3)	0.039 (3)	−0.0069 (19)	0.0036 (19)	0.006 (2)

Geometric parameters (Å, º)

S1—C4	1.7422 (14)	C9—C10	1.388 (2)
S1—C16	1.8130 (15)	C9—H9	0.99 (2)
F1—C8	1.3657 (19)	C10—H10	0.96 (2)
O1—C11	1.2133 (18)	C12—C13	1.498 (2)
O2—C11	1.3522 (18)	C12—H12A	1.00 (2)
O2—C12	1.4526 (17)	C12—H12B	0.988 (19)
O3—C17	1.2236 (17)	C13—H12C	1.03 (2)
O4—C21	1.3680 (18)	C13—H13A	1.00 (2)
O4—C24	1.426 (2)	C13—H13B	0.98 (3)
N1—C4	1.2996 (18)	C14—H14A	0.97 (2)
N1—C3	1.4058 (17)	C14—H14B	0.96 (2)
N2—C4	1.3546 (17)	C14—H14C	0.98 (2)
N2—C15	1.3963 (17)	C15—C16	1.5020 (19)
N2—C1	1.4762 (16)	C16—H16A	0.98 (2)
N3—C15	1.2750 (18)	C16—H16B	0.98 (2)
N3—N4	1.3880 (15)	C17—C18	1.4939 (19)
N4—C17	1.3698 (18)	C18—C23	1.391 (2)
N4—H4	0.885 (19)	C18—C19	1.401 (2)

C1—C2	1.5194 (18)	C19—C20	1.379 (2)
C1—C5	1.5226 (19)	C19—H19	0.96 (2)
C1—H1	0.987 (17)	C20—C21	1.392 (2)
C2—C3	1.356 (2)	C20—H20	0.97 (2)
C2—C11	1.4694 (19)	C21—C22	1.390 (2)
C3—C14	1.5024 (19)	C22—C23	1.392 (2)
C5—C10	1.391 (2)	C22—H22	0.99 (2)
C5—C6	1.392 (2)	C23—H23	0.960 (19)
C6—C7	1.392 (2)	C24—H24A	0.99 (2)
C6—H6	1.004 (19)	C24—H24B	1.00 (2)
C7—C8	1.373 (3)	C24—H24C	0.95 (2)
C7—H7	0.97 (2)	O5—H5A	0.8700
C8—C9	1.374 (3)	O5—H5B	0.8701

C4—S1—C16	92.44 (6)	C13—C12—H12B	112.3 (11)
C11—O2—C12	116.09 (11)	H12A—C12—H12B	108.7 (16)
C21—O4—C24	118.60 (14)	C12—C13—H12C	111.3 (12)
C4—N1—C3	116.27 (12)	C12—C13—H13A	107.9 (13)
C4—N2—C15	116.48 (11)	H12C—C13—H13A	110.2 (18)
C4—N2—C1	121.74 (11)	C12—C13—H13B	110.9 (14)
C15—N2—C1	121.23 (11)	H12C—C13—H13B	107.1 (18)
C15—N3—N4	115.33 (11)	H13A—C13—H13B	109.4 (19)
C17—N4—N3	116.80 (11)	C3—C14—H14A	111.4 (13)
C17—N4—H4	118.6 (12)	C3—C14—H14B	112.1 (14)
N3—N4—H4	118.8 (12)	H14A—C14—H14B	103.9 (18)
N2—C1—C2	107.75 (11)	C3—C14—H14C	109.4 (12)
N2—C1—C5	109.80 (11)	H14A—C14—H14C	109.8 (18)
C2—C1—C5	112.38 (11)	H14B—C14—H14C	110.1 (18)
N2—C1—H1	106.8 (9)	N3—C15—N2	118.03 (12)
C2—C1—H1	110.3 (9)	N3—C15—C16	130.06 (12)
C5—C1—H1	109.6 (10)	N2—C15—C16	111.90 (11)
C3—C2—C11	121.84 (12)	C15—C16—S1	106.69 (9)
C3—C2—C1	121.53 (12)	C15—C16—H16A	111.4 (12)
C11—C2—C1	116.62 (12)	S1—C16—H16A	109.4 (11)
C2—C3—N1	122.42 (12)	C15—C16—H16B	109.7 (12)
C2—C3—C14	125.10 (13)	S1—C16—H16B	109.9 (12)
N1—C3—C14	112.47 (12)	H16A—C16—H16B	109.8 (16)
N1—C4—N2	126.10 (12)	O3—C17—N4	123.09 (13)
N1—C4—S1	121.47 (10)	O3—C17—C18	121.90 (13)
N2—C4—S1	112.41 (10)	N4—C17—C18	115.00 (12)
C10—C5—C6	119.33 (14)	C23—C18—C19	118.49 (13)
C10—C5—C1	120.14 (13)	C23—C18—C17	124.17 (13)
C6—C5—C1	120.53 (13)	C19—C18—C17	117.34 (13)
C5—C6—C7	120.41 (16)	C20—C19—C18	120.67 (15)
C5—C6—H6	118.7 (11)	C20—C19—H19	120.6 (11)
C7—C6—H6	120.9 (11)	C18—C19—H19	118.8 (11)
C8—C7—C6	118.11 (15)	C19—C20—C21	120.16 (15)
C8—C7—H7	122.1 (12)	C19—C20—H20	121.9 (13)

C6—C7—H7	119.8 (12)	C21—C20—H20	117.9 (13)
F1—C8—C7	118.48 (16)	O4—C21—C22	124.66 (14)
F1—C8—C9	118.13 (17)	O4—C21—C20	115.13 (14)
C7—C8—C9	123.39 (16)	C22—C21—C20	120.20 (14)
C8—C9—C10	117.76 (17)	C21—C22—C23	119.12 (14)
C8—C9—H9	119.7 (13)	C21—C22—H22	120.7 (11)
C10—C9—H9	122.5 (13)	C23—C22—H22	120.2 (11)
C9—C10—C5	120.96 (15)	C18—C23—C22	121.34 (14)
C9—C10—H10	119.1 (12)	C18—C23—H23	120.2 (11)
C5—C10—H10	119.9 (12)	C22—C23—H23	118.4 (11)
O1—C11—O2	122.00 (13)	O4—C24—H24A	110.4 (13)
O1—C11—C2	127.18 (14)	O4—C24—H24B	110.9 (13)
O2—C11—C2	110.81 (11)	H24A—C24—H24B	110.1 (18)
O2—C12—C13	106.88 (13)	O4—C24—H24C	104.9 (13)
O2—C12—H12A	108.3 (12)	H24A—C24—H24C	111.1 (18)
C13—C12—H12A	112.1 (12)	H24B—C24—H24C	109.4 (18)
O2—C12—H12B	108.5 (11)	H5A—O5—H5B	104.0

C15—N3—N4—C17	173.45 (12)	C1—C5—C10—C9	−179.13 (15)
C4—N2—C1—C2	−21.62 (17)	C12—O2—C11—O1	1.5 (2)
C15—N2—C1—C2	167.22 (11)	C12—O2—C11—C2	−179.00 (12)
C4—N2—C1—C5	101.08 (14)	C3—C2—C11—O1	2.3 (2)
C15—N2—C1—C5	−70.08 (15)	C1—C2—C11—O1	−176.78 (15)
N2—C1—C2—C3	20.41 (18)	C3—C2—C11—O2	−177.21 (13)
C5—C1—C2—C3	−100.69 (15)	C1—C2—C11—O2	3.75 (18)
N2—C1—C2—C11	−160.54 (12)	C11—O2—C12—C13	173.66 (14)
C5—C1—C2—C11	78.36 (15)	N4—N3—C15—N2	178.26 (11)
C11—C2—C3—N1	173.50 (13)	N4—N3—C15—C16	−2.1 (2)
C1—C2—C3—N1	−7.5 (2)	C4—N2—C15—N3	177.79 (12)
C11—C2—C3—C14	−5.0 (2)	C1—N2—C15—N3	−10.60 (19)
C1—C2—C3—C14	174.03 (14)	C4—N2—C15—C16	−1.93 (17)
C4—N1—C3—C2	−7.2 (2)	C1—N2—C15—C16	169.67 (12)
C4—N1—C3—C14	171.48 (13)	N3—C15—C16—S1	−176.70 (12)
C3—N1—C4—N2	6.2 (2)	N2—C15—C16—S1	2.98 (14)
C3—N1—C4—S1	−171.99 (10)	C4—S1—C16—C15	−2.61 (11)
C15—N2—C4—N1	−178.53 (13)	N3—N4—C17—O3	−7.08 (19)
C1—N2—C4—N1	9.9 (2)	N3—N4—C17—C18	174.20 (11)
C15—N2—C4—S1	−0.18 (15)	O3—C17—C18—C23	−160.50 (14)
C1—N2—C4—S1	−171.74 (10)	N4—C17—C18—C23	18.2 (2)
C16—S1—C4—N1	−179.84 (12)	O3—C17—C18—C19	19.1 (2)
C16—S1—C4—N2	1.73 (11)	N4—C17—C18—C19	−162.14 (13)
N2—C1—C5—C10	−58.95 (16)	C23—C18—C19—C20	−1.5 (2)
C2—C1—C5—C10	60.97 (17)	C17—C18—C19—C20	178.83 (14)
N2—C1—C5—C6	121.37 (13)	C18—C19—C20—C21	1.3 (2)
C2—C1—C5—C6	−118.72 (14)	C24—O4—C21—C22	1.3 (2)
C10—C5—C6—C7	−1.9 (2)	C24—O4—C21—C20	−178.54 (16)
C1—C5—C6—C7	177.79 (13)	C19—C20—C21—O4	179.23 (14)
C5—C6—C7—C8	1.4 (2)	C19—C20—C21—C22	−0.6 (2)

C6—C7—C8—F1	179.90 (15)	O4—C21—C22—C23	−179.73 (14)
C6—C7—C8—C9	0.4 (3)	C20—C21—C22—C23	0.1 (2)
F1—C8—C9—C10	178.81 (16)	C19—C18—C23—C22	1.0 (2)
C7—C8—C9—C10	−1.7 (3)	C17—C18—C23—C22	−179.37 (13)
C8—C9—C10—C5	1.2 (3)	C21—C22—C23—C18	−0.3 (2)
C6—C5—C10—C9	0.6 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N1^{i}	0.885 (19)	2.164 (19)	2.9888 (17)	154.8 (16)
C1—H1···O5^{ii}	0.987 (17)	2.345 (18)	3.307 (5)	164.7 (13)
C7—H7···O4^{iii}	0.97 (2)	2.41 (2)	3.285 (2)	148.7 (17)
C13—H13*B*···F1^{ii}	0.98 (3)	2.49 (3)	3.386 (2)	153.0 (19)
C16—H16*A*···N1^{i}	0.98 (2)	2.58 (2)	3.4019 (19)	142.4 (15)
C16—H16*B*···O5^{iv}	0.98 (2)	2.37 (2)	3.282 (5)	154.6 (16)
C24—H24*A*···O1^{v}	0.99 (2)	2.53 (2)	3.450 (3)	154.6 (18)
C24—H24*C*···O1^{vi}	0.95 (2)	2.57 (2)	3.504 (2)	167.8 (17)
O5—H5*A*···F1	0.87	1.76	2.479 (5)	138
O5—H5*B*···O3^{vii}	0.87	2.00	2.863 (5)	174

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