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Ethyl 3-amino-4-(4-chlorophenyl)-2-[(4-methoxyphenyl)carbamoyl]-6-phenylthieno[2,3-*b*]pyridine-5-carboxylate

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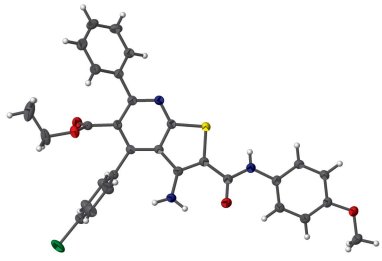
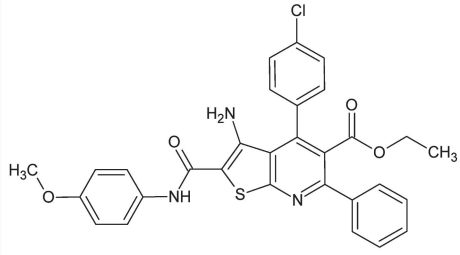
Structural data: full structural data are available from iucrdata.iucr.org

The conformation of the title molecule, $C_{30}H_{24}ClN_3O_4S$, is partially determined by an intramolecular N—H···O hydrogen bond, forming an $S(6)$ loop, and an N—H···π interaction involving the centroid of the 4-chlorophenyl ring. The thienopyridine bicyclic system is almost planar with an r.m.s. deviation of 0.019 Å. Its mean plane is inclined to the phenyl ring, the 4-chlorophenyl ring and the 4-methoxyphenyl ring by 36.19 (7), 81.67 (7) and 12.75 (7)°, respectively. In the crystal, molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(20)$ ring motif. Within the dimers, which stack along the *b*-axis direction, there is a weak π–π interaction [centroid-to-centroid distance = 3.7936 (9) Å] involving inversion-related thiophene and pyridine rings.

3D view



Chemical scheme



Structure description

Many thieno[2,3-*b*]pyridines have been synthesized and investigated in relation with their biological and pharmacological importance (Bakhite, 2003; Litvinov *et al.*, 2005). Some of them have been proved to possess antiviral (Schnute *et al.*, 2007; Attaby *et al.*, 2007), antidiabetic (Bahekar *et al.*, 2007), antimicrobial (Abdel-Rahman *et al.*, 2003; Hussein *et al.*, 2000), antitumor (Hayakawa *et al.*, 2004), antiparasitic (Bernardino *et al.*, 2006) and neurotropic activities (Krauze *et al.*,1999). We report herein on the synthesis and crystal structure of the new title thienopyridine derivative.

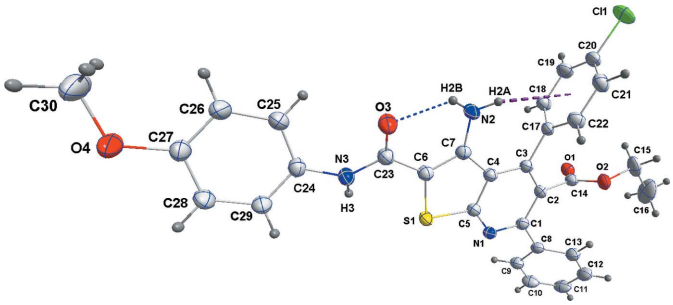


Figure 1
The molecular structure of the title compound, showing the atom labelling and 50% probability displacement ellipsoids. The N—H···O hydrogen bond and the N—H···π interaction are shown as dashed lines (see Table 1).

The conformation of the title molecule (Fig. 1) is partially determined by the intramolecular N2—H2*B*···O3 hydrogen bond and the N2—H2*A*···π interaction (H2*A*···*Cg* = 2.90 Å; N2—H2*A*···*Cg* = 152°, *Cg* is the centroid of the 4-chlorophenyl ring; see Table 1). The central thienopyridine bicyclic moiety (S1/N1/C1–C7) is planar to within 0.025 (1) Å, with an r.m.s. deviation of 0.019 Å. The phenyl ring (C8–C13) and the 4-chlorophenyl ring (C17–C22) are inclined to the aforementioned plane by 36.19 (6) and 81.67 (7)°, respectively.

In the crystal, molecules are associated through pairs of N3—H3···O1^{i} hydrogen bonds (Table 1 and Fig. 2), generating inversion dimers with an $R_2^2(20)$ loop. Within the dimers, which stack along the *b*-axis direction, there is a weak parallel slipped π–π interaction involving inversion-related thiophene and pyridine rings [*Cg*1···*Cg*2^{ii} = 3.7936 (9) Å, interplanar distance = 3.5684 (6) Å, slippage 1.371 Å, *Cg*1 and *Cg*2 are the centroids of rings S1/C4–C7 and N1/C1–C5, respectively; symmetry code: (ii) $-x+1, -y+1, -z+1$].

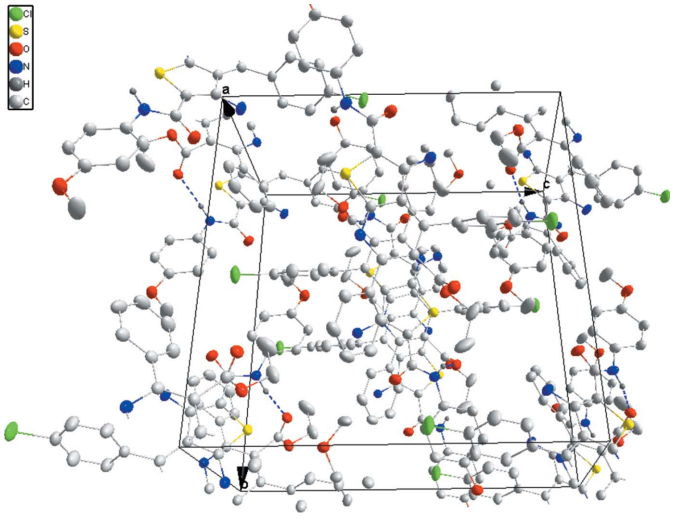


Figure 2
The crystal packing of the title compound projected onto (110), with the N—H···O hydrogen bonds shown as dashed lines (see Table 1).

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

Cg is the centroid of the C17–C22 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O3	0.88 (2)	2.07 (2)	2.756 (2)	133.6 (19)
N2—H2*A*···*Cg*	0.88 (2)	2.90	3.698	152
N3—H3···O1^{i}	0.88 (2)	2.15 (2)	2.912 (2)	145 (2)

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

Synthesis and crystallization

The title compound was prepared by heating equimolar amounts of ethyl 1,2-dihydro-4-(4-chlorophenyl)-3-cyano-6-phenyl-2-thioxopyridine-5-carboxylate and chloro-*N*-(4-methoxy-phenyl)acetamide (5 mmol) in absolute ethanol (20 ml) containing sodium ethoxide (0.5 g) on a steam bath for 30 min. The product which separated on cooling was collected and recrystallized from ethanol solution (yield: 82%) giving pale-yellow needle-like crystals.

Spectroscopic and analytical data: IR: 3500, 3300 (NH_2), 3200 (NH), 1720 (C═O, ester), 1660 (C═O, amide) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.00 (*s*, 1H, NH), 7.0–7.8 (*m*, 13H, ArH), 5.7(*s*, 2H, NH_2), 3.9–4.2 (*q*, 2H, OCH_2), 3.8 (*s*, 3H, OCH_3), 1.0–1.2 (*t*, 3H, CH_3) p.p.m. Elemental analysis calculated for $C_{31}H_{25}ClN_2O_4S$ (%): C, 66.84; H, 4.52; N, 5.03; S, 5.76. Found (%): C, 67.01; H, 4.44; N, 5.13; S, 5.49; m.p. 466–467 K.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{30}H_{24}ClN_3O_4S$
M_r	558.03
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	8.8388 (3), 17.7686 (6), 16.9487 (6)
β (°)	94.159 (2)
V (Å^3)	2654.84 (16)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.36
Crystal size (mm)	0.16 × 0.07 × 0.07
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.75, 0.85
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20325, 5277, 4468
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.094, 1.02
No. of reflections	5277
No. of parameters	367
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.22

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160657 [doi:10.1107/S241431461600657X]

Ethyl 3-amino-4-(4-chlorophenyl)-2-[(4-methoxyphenyl)carbamoyl]-6-phenylthieno[2,3-*b*]pyridine-5-carboxylate

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Crystal data

$C_{30}H_{24}ClN_3O_4S$
M_r = 558.03
Monoclinic, $P2_1/c$
a = 8.8388 (3) Å
b = 17.7686 (6) Å
c = 16.9487 (6) Å
β = 94.159 (2)°
V = 2654.84 (16) Å^3
Z = 4
$F(000)$ = 1160
D_x = 1.396 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9974 reflections
θ = 3.6–74.3°
μ = 2.36 mm^{-1}
T = 150 K
Needle, pale-yellow
0.16 × 0.07 × 0.07 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*; Bruker, 2016)
T_{min} = 0.75, T_{max} = 0.85
20325 measured reflections
5277 independent reflections
4468 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 74.5°, θ_{min} = 3.6°
h = −11→10
k = −19→22
l = −17→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.02
5277 reflections
367 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 1.0305P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00154 (15)

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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.93057 (7)	0.55123 (3)	0.07821 (3)	0.05299 (16)
S1	0.61224 (5)	0.59156 (2)	0.59762 (2)	0.02643 (11)
O1	0.74915 (13)	0.32446 (7)	0.34507 (7)	0.0320 (3)
O2	0.98542 (13)	0.37180 (7)	0.36461 (7)	0.0322 (3)
O3	0.64084 (15)	0.78617 (7)	0.48736 (7)	0.0366 (3)
O4	0.31751 (16)	1.03614 (7)	0.69484 (8)	0.0399 (3)
N1	0.70552 (15)	0.45194 (7)	0.56600 (7)	0.0254 (3)
N2	0.70828 (18)	0.66939 (9)	0.38878 (9)	0.0333 (3)
H2A	0.763 (2)	0.6506 (13)	0.3521 (13)	0.044 (6)*
H2B	0.704 (2)	0.7185 (14)	0.3956 (13)	0.048 (6)*
N3	0.50338 (17)	0.75521 (8)	0.59171 (8)	0.0295 (3)
H3	0.461 (3)	0.7179 (13)	0.6165 (13)	0.049 (6)*
C1	0.76387 (17)	0.40248 (9)	0.51642 (9)	0.0247 (3)
C2	0.79742 (17)	0.42332 (9)	0.43908 (9)	0.0245 (3)
C3	0.77840 (17)	0.49702 (9)	0.41263 (9)	0.0237 (3)
C4	0.72153 (17)	0.54956 (9)	0.46494 (9)	0.0237 (3)
C5	0.68559 (17)	0.52221 (9)	0.53961 (9)	0.0241 (3)
C6	0.63015 (18)	0.65820 (9)	0.52280 (9)	0.0268 (3)
C7	0.68925 (18)	0.62898 (9)	0.45635 (9)	0.0261 (3)
C8	0.79395 (19)	0.32535 (9)	0.54762 (9)	0.0269 (3)
C9	0.6953 (2)	0.29235 (10)	0.59818 (10)	0.0314 (4)
H9	0.6103	0.3196	0.6141	0.038*
C10	0.7224 (2)	0.21932 (10)	0.62509 (11)	0.0401 (4)
H10	0.6550	0.1966	0.6592	0.048*
C11	0.8467 (3)	0.17944 (10)	0.60255 (11)	0.0427 (5)
H11	0.8627	0.1291	0.6201	0.051*
C12	0.9478 (2)	0.21265 (11)	0.55452 (11)	0.0407 (4)
H12	1.0343	0.1856	0.5401	0.049*
C13	0.9221 (2)	0.28560 (10)	0.52754 (10)	0.0341 (4)
H13	0.9922	0.3087	0.4952	0.041*
C14	0.83919 (18)	0.36646 (9)	0.37896 (9)	0.0260 (3)
C15	1.0348 (2)	0.32705 (13)	0.29932 (12)	0.0469 (5)
H15A	1.1261	0.3504	0.2792	0.056*
H15B	0.9539	0.3268	0.2557	0.056*

C16	1.0705 (3)	0.24785 (15)	0.32371 (17)	0.0703 (8)
H16A	1.1103	0.2206	0.2794	0.105*
H16B	0.9780	0.2231	0.3390	0.105*
H16C	1.1466	0.2479	0.3687	0.105*
C17	0.81286 (17)	0.51549 (9)	0.32963 (9)	0.0244 (3)
C18	0.70985 (19)	0.49708 (10)	0.26706 (10)	0.0313 (4)
H18	0.6144	0.4761	0.2773	0.038*
C19	0.7451 (2)	0.50915 (11)	0.18947 (10)	0.0363 (4)
H19	0.6740	0.4969	0.1467	0.044*
C20	0.8838 (2)	0.53903 (10)	0.17525 (10)	0.0320 (4)
C21	0.9873 (2)	0.55861 (11)	0.23643 (11)	0.0367 (4)
H21	1.0821	0.5801	0.2257	0.044*
C22	0.9521 (2)	0.54672 (10)	0.31378 (10)	0.0332 (4)
H22	1.0232	0.5599	0.3562	0.040*
C23	0.59152 (19)	0.73833 (9)	0.53178 (9)	0.0279 (3)
C24	0.45659 (18)	0.82863 (9)	0.61364 (10)	0.0277 (3)
C25	0.4291 (2)	0.88638 (10)	0.55940 (10)	0.0306 (4)
H25	0.4431	0.8781	0.5050	0.037*
C26	0.3810 (2)	0.95634 (10)	0.58454 (10)	0.0319 (4)
H26	0.3626	0.9959	0.5473	0.038*
C27	0.35998 (19)	0.96856 (9)	0.66361 (10)	0.0295 (4)
C28	0.3847 (2)	0.91026 (10)	0.71805 (10)	0.0313 (4)
H28	0.3687	0.9182	0.7722	0.038*
C29	0.43253 (19)	0.84107 (9)	0.69294 (10)	0.0300 (4)
H29	0.4493	0.8014	0.7301	0.036*
C30	0.2967 (3)	1.09714 (12)	0.64081 (14)	0.0578 (7)
H30A	0.2724	1.1429	0.6697	0.087*
H30B	0.2133	1.0855	0.6014	0.087*
H30C	0.3901	1.1051	0.6141	0.087*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0659 (3)	0.0684 (4)	0.0269 (2)	−0.0027 (3)	0.0192 (2)	0.0049 (2)
S1	0.0347 (2)	0.0231 (2)	0.0222 (2)	0.00087 (15)	0.00689 (14)	0.00014 (14)
O1	0.0371 (6)	0.0291 (6)	0.0303 (6)	−0.0034 (5)	0.0048 (5)	−0.0045 (5)
O2	0.0303 (6)	0.0372 (7)	0.0298 (6)	0.0027 (5)	0.0067 (5)	−0.0067 (5)
O3	0.0489 (7)	0.0249 (6)	0.0383 (7)	0.0011 (5)	0.0182 (6)	0.0045 (5)
O4	0.0604 (8)	0.0258 (6)	0.0358 (7)	0.0099 (6)	0.0179 (6)	0.0026 (5)
N1	0.0294 (7)	0.0247 (7)	0.0219 (6)	−0.0003 (5)	0.0013 (5)	0.0007 (5)
N2	0.0491 (9)	0.0246 (8)	0.0280 (8)	0.0039 (7)	0.0146 (6)	0.0050 (6)
N3	0.0384 (8)	0.0217 (7)	0.0295 (7)	−0.0007 (6)	0.0106 (6)	0.0003 (5)
C1	0.0266 (8)	0.0249 (8)	0.0222 (8)	−0.0003 (6)	−0.0001 (6)	−0.0003 (6)
C2	0.0262 (8)	0.0259 (8)	0.0216 (7)	0.0019 (6)	0.0021 (6)	−0.0014 (6)
C3	0.0244 (7)	0.0258 (8)	0.0210 (7)	−0.0004 (6)	0.0016 (5)	0.0006 (6)
C4	0.0256 (7)	0.0241 (8)	0.0216 (7)	−0.0005 (6)	0.0030 (6)	0.0019 (6)
C5	0.0267 (7)	0.0245 (8)	0.0213 (7)	−0.0008 (6)	0.0022 (6)	−0.0004 (6)
C6	0.0314 (8)	0.0241 (8)	0.0253 (8)	−0.0008 (6)	0.0049 (6)	0.0014 (6)

C7	0.0281 (8)	0.0251 (8)	0.0255 (8)	0.0003 (6)	0.0042 (6)	0.0021 (6)
C8	0.0349 (8)	0.0250 (8)	0.0201 (7)	0.0020 (7)	−0.0023 (6)	−0.0001 (6)
C9	0.0409 (9)	0.0287 (9)	0.0243 (8)	0.0003 (7)	0.0003 (7)	0.0008 (6)
C10	0.0564 (12)	0.0317 (9)	0.0316 (9)	−0.0057 (8)	−0.0012 (8)	0.0070 (7)
C11	0.0667 (13)	0.0251 (9)	0.0345 (10)	0.0073 (9)	−0.0074 (9)	0.0028 (7)
C12	0.0530 (12)	0.0352 (10)	0.0332 (9)	0.0158 (9)	−0.0020 (8)	−0.0001 (8)
C13	0.0409 (10)	0.0332 (9)	0.0280 (9)	0.0076 (8)	0.0012 (7)	0.0020 (7)
C14	0.0313 (8)	0.0246 (8)	0.0225 (8)	0.0021 (6)	0.0039 (6)	0.0021 (6)
C15	0.0409 (10)	0.0611 (13)	0.0406 (11)	0.0006 (9)	0.0151 (8)	−0.0203 (9)
C16	0.0657 (16)	0.0581 (15)	0.0864 (19)	0.0208 (12)	0.0002 (13)	−0.0338 (14)
C17	0.0282 (8)	0.0238 (7)	0.0218 (7)	0.0027 (6)	0.0055 (6)	0.0008 (6)
C18	0.0281 (8)	0.0390 (9)	0.0269 (8)	−0.0030 (7)	0.0037 (6)	0.0032 (7)
C19	0.0375 (9)	0.0473 (11)	0.0237 (8)	−0.0020 (8)	0.0003 (7)	0.0000 (7)
C20	0.0394 (9)	0.0329 (9)	0.0247 (8)	0.0037 (7)	0.0103 (7)	0.0026 (7)
C21	0.0309 (9)	0.0447 (11)	0.0356 (10)	−0.0041 (8)	0.0104 (7)	0.0037 (8)
C22	0.0306 (9)	0.0400 (10)	0.0291 (9)	−0.0052 (7)	0.0025 (7)	0.0016 (7)
C23	0.0334 (8)	0.0243 (8)	0.0263 (8)	−0.0008 (6)	0.0052 (6)	−0.0003 (6)
C24	0.0309 (8)	0.0224 (8)	0.0302 (8)	0.0001 (6)	0.0055 (6)	−0.0018 (6)
C25	0.0378 (9)	0.0305 (9)	0.0239 (8)	0.0037 (7)	0.0042 (6)	0.0005 (6)
C26	0.0380 (9)	0.0292 (9)	0.0289 (9)	0.0065 (7)	0.0048 (7)	0.0039 (7)
C27	0.0345 (9)	0.0239 (8)	0.0310 (9)	0.0033 (7)	0.0076 (7)	−0.0007 (6)
C28	0.0408 (9)	0.0293 (9)	0.0248 (8)	0.0013 (7)	0.0096 (7)	0.0005 (6)
C29	0.0390 (9)	0.0250 (8)	0.0267 (8)	0.0004 (7)	0.0069 (7)	0.0034 (6)
C30	0.0977 (19)	0.0300 (10)	0.0491 (13)	0.0253 (11)	0.0278 (12)	0.0084 (9)

Geometric parameters (Å, º)

Cl1—C20	1.7383 (17)	C11—H11	0.9500
S1—C5	1.7314 (16)	C12—C13	1.388 (2)
S1—C6	1.7504 (16)	C12—H12	0.9500
O1—C14	1.206 (2)	C13—H13	0.9500
O2—C14	1.336 (2)	C15—C16	1.494 (4)
O2—C15	1.455 (2)	C15—H15A	0.9900
O3—C23	1.236 (2)	C15—H15B	0.9900
O4—C27	1.375 (2)	C16—H16A	0.9800
O4—C30	1.422 (2)	C16—H16B	0.9800
N1—C5	1.334 (2)	C16—H16C	0.9800
N1—C1	1.344 (2)	C17—C18	1.386 (2)
N2—C7	1.372 (2)	C17—C22	1.394 (2)
N2—H2A	0.88 (2)	C18—C19	1.390 (2)
N2—H2B	0.88 (2)	C18—H18	0.9500
N3—C23	1.358 (2)	C19—C20	1.373 (3)
N3—C24	1.426 (2)	C19—H19	0.9500
N3—H3	0.88 (2)	C20—C21	1.377 (3)
C1—C2	1.414 (2)	C21—C22	1.386 (2)
C1—C8	1.486 (2)	C21—H21	0.9500
C2—C3	1.390 (2)	C22—H22	0.9500
C2—C14	1.500 (2)	C24—C25	1.387 (2)

C3—C4	1.405 (2)	C24—C29	1.394 (2)
C3—C17	1.497 (2)	C25—C26	1.391 (2)
C4—C5	1.413 (2)	C25—H25	0.9500
C4—C7	1.445 (2)	C26—C27	1.383 (2)
C6—C7	1.377 (2)	C26—H26	0.9500
C6—C23	1.475 (2)	C27—C28	1.394 (2)
C8—C9	1.395 (2)	C28—C29	1.377 (2)
C8—C13	1.398 (2)	C28—H28	0.9500
C9—C10	1.390 (2)	C29—H29	0.9500
C9—H9	0.9500	C30—H30A	0.9800
C10—C11	1.385 (3)	C30—H30B	0.9800
C10—H10	0.9500	C30—H30C	0.9800
C11—C12	1.384 (3)		

C5—S1—C6	90.74 (7)	O2—C15—H15B	109.2
C14—O2—C15	116.56 (13)	C16—C15—H15B	109.2
C27—O4—C30	116.34 (14)	H15A—C15—H15B	107.9
C5—N1—C1	116.72 (13)	C15—C16—H16A	109.5
C7—N2—H2A	119.9 (15)	C15—C16—H16B	109.5
C7—N2—H2B	113.5 (15)	H16A—C16—H16B	109.5
H2A—N2—H2B	120 (2)	C15—C16—H16C	109.5
C23—N3—C24	126.17 (14)	H16A—C16—H16C	109.5
C23—N3—H3	118.5 (15)	H16B—C16—H16C	109.5
C24—N3—H3	114.9 (15)	C18—C17—C22	119.13 (15)
N1—C1—C2	121.60 (14)	C18—C17—C3	120.01 (14)
N1—C1—C8	116.57 (14)	C22—C17—C3	120.73 (14)
C2—C1—C8	121.82 (14)	C17—C18—C19	120.50 (16)
C3—C2—C1	121.13 (14)	C17—C18—H18	119.7
C3—C2—C14	116.44 (14)	C19—C18—H18	119.7
C1—C2—C14	122.13 (14)	C20—C19—C18	119.34 (16)
C2—C3—C4	117.55 (14)	C20—C19—H19	120.3
C2—C3—C17	118.78 (14)	C18—C19—H19	120.3
C4—C3—C17	123.62 (14)	C19—C20—C21	121.23 (16)
C3—C4—C5	116.78 (14)	C19—C20—Cl1	119.40 (14)
C3—C4—C7	131.47 (14)	C21—C20—Cl1	119.36 (14)
C5—C4—C7	111.75 (14)	C20—C21—C22	119.42 (16)
N1—C5—C4	126.12 (14)	C20—C21—H21	120.3
N1—C5—S1	121.45 (12)	C22—C21—H21	120.3
C4—C5—S1	112.43 (12)	C21—C22—C17	120.36 (16)
C7—C6—C23	123.57 (14)	C21—C22—H22	119.8
C7—C6—S1	113.39 (12)	C17—C22—H22	119.8
C23—C6—S1	123.00 (12)	O3—C23—N3	123.41 (15)
N2—C7—C6	124.19 (15)	O3—C23—C6	120.45 (15)
N2—C7—C4	124.04 (15)	N3—C23—C6	116.12 (14)
C6—C7—C4	111.70 (14)	C25—C24—C29	119.35 (15)
C9—C8—C13	119.38 (15)	C25—C24—N3	122.96 (15)
C9—C8—C1	120.17 (15)	C29—C24—N3	117.64 (15)
C13—C8—C1	120.44 (15)	C24—C25—C26	120.06 (16)

C10—C9—C8	119.59 (17)	C24—C25—H25	120.0
C10—C9—H9	120.2	C26—C25—H25	120.0
C8—C9—H9	120.2	C27—C26—C25	120.17 (16)
C11—C10—C9	120.53 (18)	C27—C26—H26	119.9
C11—C10—H10	119.7	C25—C26—H26	119.9
C9—C10—H10	119.7	O4—C27—C26	124.71 (15)
C12—C11—C10	120.22 (17)	O4—C27—C28	115.35 (15)
C12—C11—H11	119.9	C26—C27—C28	119.93 (15)
C10—C11—H11	119.9	C29—C28—C27	119.72 (15)
C11—C12—C13	119.68 (18)	C29—C28—H28	120.1
C11—C12—H12	120.2	C27—C28—H28	120.1
C13—C12—H12	120.2	C28—C29—C24	120.74 (15)
C12—C13—C8	120.51 (18)	C28—C29—H29	119.6
C12—C13—H13	119.7	C24—C29—H29	119.6
C8—C13—H13	119.7	O4—C30—H30A	109.5
O1—C14—O2	124.83 (15)	O4—C30—H30B	109.5
O1—C14—C2	123.65 (15)	H30A—C30—H30B	109.5
O2—C14—C2	111.40 (13)	O4—C30—H30C	109.5
O2—C15—C16	111.91 (18)	H30A—C30—H30C	109.5
O2—C15—H15A	109.2	H30B—C30—H30C	109.5
C16—C15—H15A	109.2		

C5—N1—C1—C2	−2.2 (2)	C1—C8—C13—C12	−177.88 (16)
C5—N1—C1—C8	176.70 (14)	C15—O2—C14—O1	4.6 (2)
N1—C1—C2—C3	3.3 (2)	C15—O2—C14—C2	−171.53 (15)
C8—C1—C2—C3	−175.53 (14)	C3—C2—C14—O1	−99.45 (19)
N1—C1—C2—C14	−170.19 (14)	C1—C2—C14—O1	74.3 (2)
C8—C1—C2—C14	11.0 (2)	C3—C2—C14—O2	76.68 (17)
C1—C2—C3—C4	−1.4 (2)	C1—C2—C14—O2	−109.56 (17)
C14—C2—C3—C4	172.46 (14)	C14—O2—C15—C16	−83.3 (2)
C1—C2—C3—C17	−178.82 (14)	C2—C3—C17—C18	77.9 (2)
C14—C2—C3—C17	−5.0 (2)	C4—C3—C17—C18	−99.37 (19)
C2—C3—C4—C5	−1.3 (2)	C2—C3—C17—C22	−97.89 (19)
C17—C3—C4—C5	176.03 (14)	C4—C3—C17—C22	84.8 (2)
C2—C3—C4—C7	179.85 (16)	C22—C17—C18—C19	0.4 (3)
C17—C3—C4—C7	−2.8 (3)	C3—C17—C18—C19	−175.48 (16)
C1—N1—C5—C4	−0.7 (2)	C17—C18—C19—C20	0.5 (3)
C1—N1—C5—S1	−179.70 (11)	C18—C19—C20—C21	−1.3 (3)
C3—C4—C5—N1	2.5 (2)	C18—C19—C20—Cl1	177.86 (14)
C7—C4—C5—N1	−178.43 (15)	C19—C20—C21—C22	1.2 (3)
C3—C4—C5—S1	−178.46 (11)	Cl1—C20—C21—C22	−177.99 (15)
C7—C4—C5—S1	0.62 (17)	C20—C21—C22—C17	−0.2 (3)
C6—S1—C5—N1	178.69 (14)	C18—C17—C22—C21	−0.5 (3)
C6—S1—C5—C4	−0.41 (12)	C3—C17—C22—C21	175.32 (16)
C5—S1—C6—C7	0.08 (13)	C24—N3—C23—O3	−1.1 (3)
C5—S1—C6—C23	−177.49 (14)	C24—N3—C23—C6	177.44 (15)
C23—C6—C7—N2	−5.2 (3)	C7—C6—C23—O3	−16.0 (3)
S1—C6—C7—N2	177.27 (13)	S1—C6—C23—O3	161.36 (13)

C23—C6—C7—C4	177.81 (15)	C7—C6—C23—N3	165.42 (16)
S1—C6—C7—C4	0.25 (18)	S1—C6—C23—N3	−17.3 (2)
C3—C4—C7—N2	1.3 (3)	C23—N3—C24—C25	32.6 (3)
C5—C4—C7—N2	−177.58 (15)	C23—N3—C24—C29	−149.90 (17)
C3—C4—C7—C6	178.34 (16)	C29—C24—C25—C26	1.3 (3)
C5—C4—C7—C6	−0.56 (19)	N3—C24—C25—C26	178.83 (16)
N1—C1—C8—C9	36.8 (2)	C24—C25—C26—C27	−0.2 (3)
C2—C1—C8—C9	−144.34 (16)	C30—O4—C27—C26	−1.0 (3)
N1—C1—C8—C13	−142.32 (16)	C30—O4—C27—C28	177.92 (19)
C2—C1—C8—C13	36.5 (2)	C25—C26—C27—O4	177.84 (17)
C13—C8—C9—C10	−2.7 (2)	C25—C26—C27—C28	−1.0 (3)
C1—C8—C9—C10	178.12 (15)	O4—C27—C28—C29	−177.85 (16)
C8—C9—C10—C11	0.5 (3)	C26—C27—C28—C29	1.1 (3)
C9—C10—C11—C12	1.7 (3)	C27—C28—C29—C24	0.0 (3)
C10—C11—C12—C13	−1.4 (3)	C25—C24—C29—C28	−1.2 (3)
C11—C12—C13—C8	−0.9 (3)	N3—C24—C29—C28	−178.88 (16)
C9—C8—C13—C12	3.0 (3)		

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C17–C22 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O3	0.88 (2)	2.07 (2)	2.756 (2)	133.6 (19)
N2—H2*A*···*Cg*	0.88 (2)	2.90	3.698	152
N3—H3···O1^{i}	0.88 (2)	2.15 (2)	2.912 (2)	145 (2)

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