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Ethyl 13-(4-chlorophenyl)-11-methyl-6-oxo-5-phenyl-8-thia-3,4,5,10-tetraazatricyclo[7.4.0.0^{2,7}]-trideca-1(9),2(7),3,10,12-pentaene-12-carboxylate

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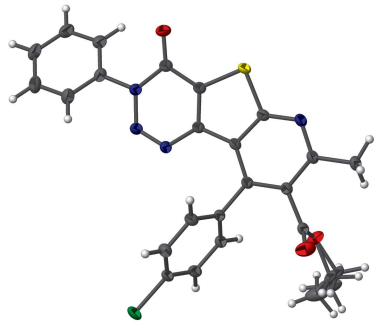
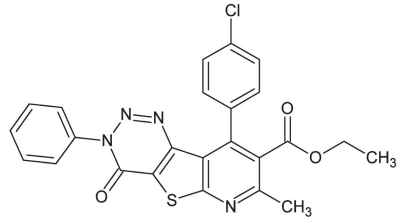
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{24}H_{17}ClN_4O_3S$, the central tricyclic moiety is twisted slightly, as indicated by the dihedral angles of 4.86 (5) and 0.97 (6)°, respectively, between the five-membered ring and the C_3N_3 and pyridyl rings. Additionally, the chlorobenzene ring makes a dihedral angle of 65.80 (5)° with the pyridyl ring. Weak C—H···O, C—Cl···N [3.0239 (13) Å] and π–π stacking interactions [inter-centroid distance between thienyl rings = 3.6994 (8) Å, and between thienyl and pyridyl rings = 3.7074 (8) Å] contribute to the molecular packing. The ethyl group in the ester moiety is disordered over two sets of sites, with the major component having an occupancy of 0.567 (11).

3D view



Chemical scheme



Structure description

Among heterocyclic systems, thienopyridines attract considerable attention due to their various biological activities and pharmaceutical properties (Litvinov *et al.*, 2005; Mohamed *et al.*, 2007; Bakhite, 2003). Thienopyridines have been reported to be anti-malarial (Görlitzer *et al.*, 2004), anti-platelet (Girija *et al.*, 2011) and anti-microbial agents. As part of our studies in this area, we report here the synthesis and the crystal structure of the title compound (Fig. 1).

The central tricyclic moiety is twisted slightly, as indicated by the dihedral angles of 4.86 (5) and 0.97 (6)°, respectively, between the five-membered ring and the C_3N_3 and pyridyl rings. Additionally, the 4-chlorobenzene ring makes a dihedral angle of 65.80 (5)° with the pyridyl ring.

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O2^{i}	0.99	2.42	3.339 (7)	154

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

In the crystal, weak C8—H8A···O1^{i} hydrogen bonds (Table 1) form chains parallel to (100). Intercalation of adjacent chains is aided by slipped π–π stacking interactions between centrosymmetrically related thienyl rings [inter-centroid distance = 3.6994 (8) Å; $-x$, $-y$, $1-z$] and the between thienyl and pyridyl rings [inter-centroid distance = 3.7074 (8) Å; $-x$, $1-y$, $1-z$]. In the latter interaction, the dihedral angle between the planes is 0.97 (7)°. This intercalation forms sheets which are associated through Cl1—N1($-1+x$, y, z) interactions with Cl···N distances of 3.024 (1) Å. This is 0.28 Å less than the sum of the corresponding van der Waals radii and is thus considered to be an attractive interaction. The ethyl group of the ester is disordered over two sets of sites by a rotation of approximately 13° about the C7—O3 bond.

Synthesis and crystallization

The title compound was synthesized according to our reported method (Mohamed *et al.*, 2007). Single crystals of the title compound were obtained by recrystallization from an ethanol solution to afford colourless plates suitable for X-ray diffraction. Yield (81%); M.p. 453–454 K. IR: 1720 (C═O, ester), 1660 (C═O, triazinone) cm$^{-1.}$ ^{1}H NMR ($CDCl_3$): δ = 7.1–7.6 (*m*, 9H, ArH), 4.1 (*q*, 2H, OCH_2), 2.7 (*s*, 3H, CH_3 at C-7), 1.1 (*t*, 3H, CH_3 of ester group).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.The ethyl group in the ester moiety is disordered over two sets of sites in approximately equal amounts; major component = 0.567 (11). The two components of the disorder were refined with restraints so that their geometries are comparable.

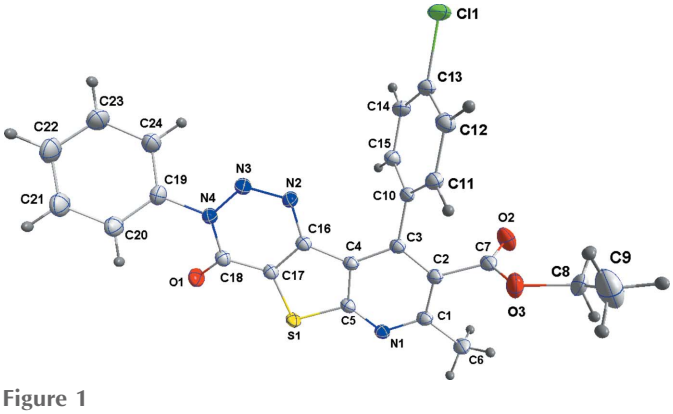


Figure 1
Perspective view of the title molecule with labelling scheme and 50% probability ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{17}ClN_4O_3S$
M_r	476.92
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	11.8562 (3), 7.1984 (2), 25.4331 (5)
β (°)	101.045 (1)
V (Å^3)	2130.40 (9)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.81
Crystal size (mm)	0.22 × 0.17 × 0.06
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.73, 0.85
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15584, 4116, 3824
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.083, 1.02
No. of reflections	4116
No. of parameters	309
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.25

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

Acknowledgements

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References

Bakhite, E. A. (2003). *Phosphorus Sulfur Silicon*, **178**, 929–992.
Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Girija, D., Singh, B. D. & Komal, S. (2011). *J. Drug Deliv. Therapeut.* **1**, 8–16.
Görlitzer, K., Meyer, H., Walter, R. D., Jomaa, H. & Wiesner, J. (2004). *Pharmazie*, **59**, 506–512.
Litvinov, V. P., Dotsenko, V. V. & Krivokolysko, S. G. (2005). *Russ. Chem. Bull.* **54**, 864–904.
Mohamed, O. S., Al-Taifi, E. A., El-Emary, T. I. & Bakhite, E. A.-G. (2007). *Phosphorus Sulfur Silicon*, **182**, 1061–1082.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2016). **1**, x160701 [doi:10.1107/S241431461600701X]

Ethyl 13-(4-chlorophenyl)-11-methyl-6-oxo-5-phenyl-8-thia-3,4,5,10-tetraazatricyclo[7.4.0.0^{2,7}]trideca-1(9),2(7),3,10,12-pentaene-12-carboxylate

Elham A. Al-Taifi, Joel T. Mague, Shaaban K. Mohamed, Mehmet Akkurt and Etify A. Bakhite

Ethyl 13-(4-chlorophenyl)-11-methyl-6-oxo-5-phenyl-8-thia-3,4,5,10-tetraazatricyclo[7.4.0.0^{2,7}]trideca-1(9),2(7),3,10,12-pentaene-12-carboxylate

Crystal data

$C_{24}H_{17}ClN_4O_3S$
M_r = 476.92
Monoclinic, $P2_1/n$
a = 11.8562 (3) Å
b = 7.1984 (2) Å
c = 25.4331 (5) Å
β = 101.045 (1)°
V = 2130.40 (9) Å^3
Z = 4
$F(000)$ = 984
D_x = 1.487 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9972 reflections
θ = 3.5–72.3°
μ = 2.81 mm^{-1}
T = 150 K
Tablet, colourless
0.22 × 0.17 × 0.06 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} = 0.73, T_{max} = 0.85
15584 measured reflections
4116 independent reflections
3824 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 72.4°, θ_{min} = 3.5°
h = −14→14
k = −8→8
l = −30→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.02
4116 reflections
309 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 1.0088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015a), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00183 (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. The ethyl group in the ester moiety is disordered over two sites in approximately equal amounts. The two components of the disorder were refined with restraints that their geometries be comparable.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.71998 (3)	0.29217 (6)	0.56218 (2)	0.02941 (11)	
S1	−0.07638 (3)	0.19406 (5)	0.46290 (2)	0.02105 (11)	
O1	−0.05465 (9)	0.03663 (16)	0.34942 (4)	0.0281 (2)	
O2	0.29995 (10)	0.35512 (17)	0.69010 (5)	0.0377 (3)	
O3	0.25376 (10)	0.63799 (16)	0.65508 (4)	0.0341 (3)	
N1	−0.02471 (10)	0.31809 (17)	0.56408 (5)	0.0214 (3)	
N2	0.24293 (10)	0.21959 (17)	0.44231 (5)	0.0218 (3)	
N3	0.23889 (10)	0.17642 (18)	0.39328 (5)	0.0233 (3)	
N4	0.13775 (10)	0.11843 (17)	0.36123 (5)	0.0215 (3)	
C1	0.05229 (12)	0.3755 (2)	0.60634 (5)	0.0212 (3)	
C2	0.17099 (11)	0.3855 (2)	0.60556 (5)	0.0201 (3)	
C3	0.21389 (11)	0.33098 (19)	0.56076 (5)	0.0189 (3)	
C4	0.13238 (11)	0.27512 (19)	0.51566 (5)	0.0185 (3)	
C5	0.01653 (11)	0.27172 (19)	0.52070 (5)	0.0194 (3)	
C6	0.00673 (13)	0.4217 (2)	0.65600 (6)	0.0275 (3)	
H6A	−0.0765	0.4408	0.6466	0.041*	
H6B	0.0436	0.5354	0.6721	0.041*	
H6C	0.0234	0.3192	0.6816	0.041*	
C7	0.24994 (11)	0.4536 (2)	0.65525 (5)	0.0227 (3)	
C8	0.3101 (7)	0.7424 (11)	0.70277 (19)	0.0316 (14)	0.567 (11)
H8A	0.2540	0.7684	0.7261	0.038*	0.567 (11)
H8B	0.3736	0.6680	0.7234	0.038*	0.567 (11)
C9	0.3541 (7)	0.9138 (10)	0.6860 (3)	0.0541 (14)	0.567 (11)
H9A	0.4033	0.8878	0.6600	0.081*	0.567 (11)
H9B	0.3990	0.9775	0.7171	0.081*	0.567 (11)
H9C	0.2899	0.9932	0.6693	0.081*	0.567 (11)
C8A	0.3320 (9)	0.7159 (15)	0.7019 (3)	0.0316 (14)	0.433 (11)
H8C	0.2872	0.7612	0.7284	0.038*	0.433 (11)
H8D	0.3854	0.6184	0.7192	0.038*	0.433 (11)
C9A	0.3961 (9)	0.8666 (14)	0.6850 (4)	0.0541 (14)	0.433 (11)
H9D	0.4612	0.8170	0.6708	0.081*	0.433 (11)
H9E	0.4245	0.9478	0.7156	0.081*	0.433 (11)

H9F	0.3461	0.9380	0.6570	0.081*	0.433 (11)
C10	0.33982 (11)	0.3247 (2)	0.56127 (5)	0.0197 (3)	
C11	0.40585 (12)	0.4854 (2)	0.56597 (5)	0.0215 (3)	
H11	0.3707	0.6024	0.5691	0.026*	
C12	0.52335 (12)	0.4761 (2)	0.56616 (6)	0.0242 (3)	
H12	0.5684	0.5860	0.5689	0.029*	
C13	0.57320 (12)	0.3046 (2)	0.56232 (5)	0.0231 (3)	
C14	0.50944 (12)	0.1421 (2)	0.55833 (6)	0.0259 (3)	
H14	0.5454	0.0250	0.5564	0.031*	
C15	0.39210 (12)	0.1534 (2)	0.55720 (6)	0.0245 (3)	
H15	0.3471	0.0434	0.5536	0.029*	
C16	0.14303 (11)	0.21819 (19)	0.46256 (5)	0.0190 (3)	
C17	0.03916 (12)	0.1688 (2)	0.43152 (5)	0.0200 (3)	
C18	0.03111 (12)	0.1005 (2)	0.37788 (5)	0.0214 (3)	
C19	0.15161 (13)	0.0795 (2)	0.30702 (6)	0.0241 (3)	
C20	0.06189 (13)	0.1114 (2)	0.26393 (6)	0.0286 (3)	
H20	−0.0113	0.1500	0.2698	0.034*	
C21	0.08119 (15)	0.0859 (3)	0.21222 (6)	0.0343 (4)	
H21	0.0203	0.1059	0.1826	0.041*	
C22	0.18800 (15)	0.0317 (2)	0.20337 (6)	0.0359 (4)	
H22	0.2007	0.0160	0.1679	0.043*	
C23	0.27619 (15)	0.0005 (3)	0.24668 (6)	0.0352 (4)	
H23	0.3497	−0.0359	0.2407	0.042*	
C24	0.25848 (14)	0.0218 (2)	0.29868 (6)	0.0303 (3)	
H24	0.3188	−0.0028	0.3283	0.036*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01424 (17)	0.0434 (2)	0.0316 (2)	0.00137 (14)	0.00669 (13)	0.00109 (15)
S1	0.01390 (17)	0.02804 (19)	0.02085 (18)	−0.00149 (12)	0.00243 (12)	0.00103 (13)
O1	0.0230 (5)	0.0360 (6)	0.0239 (5)	−0.0074 (4)	0.0006 (4)	−0.0033 (4)
O2	0.0383 (6)	0.0409 (7)	0.0284 (6)	−0.0021 (5)	−0.0077 (5)	0.0051 (5)
O3	0.0440 (7)	0.0310 (6)	0.0232 (5)	−0.0001 (5)	−0.0040 (5)	−0.0060 (5)
N1	0.0167 (5)	0.0269 (6)	0.0214 (6)	0.0013 (5)	0.0058 (4)	0.0016 (5)
N2	0.0185 (6)	0.0290 (6)	0.0186 (6)	−0.0021 (5)	0.0055 (4)	−0.0012 (5)
N3	0.0188 (6)	0.0308 (6)	0.0204 (6)	−0.0025 (5)	0.0037 (4)	−0.0014 (5)
N4	0.0193 (6)	0.0267 (6)	0.0184 (6)	−0.0013 (5)	0.0032 (4)	−0.0008 (5)
C1	0.0190 (6)	0.0244 (7)	0.0213 (7)	0.0021 (5)	0.0062 (5)	0.0022 (6)
C2	0.0181 (6)	0.0237 (7)	0.0187 (6)	0.0019 (5)	0.0040 (5)	0.0014 (5)
C3	0.0169 (6)	0.0214 (7)	0.0186 (6)	0.0004 (5)	0.0040 (5)	0.0024 (5)
C4	0.0155 (6)	0.0206 (7)	0.0196 (6)	0.0006 (5)	0.0042 (5)	0.0027 (5)
C5	0.0160 (6)	0.0213 (7)	0.0205 (6)	0.0003 (5)	0.0025 (5)	0.0024 (5)
C6	0.0227 (7)	0.0383 (8)	0.0235 (7)	0.0017 (6)	0.0094 (6)	−0.0028 (6)
C7	0.0182 (6)	0.0325 (8)	0.0185 (6)	−0.0001 (6)	0.0062 (5)	−0.0006 (6)
C8	0.034 (3)	0.034 (2)	0.0244 (8)	0.006 (2)	0.0007 (11)	−0.0152 (9)
C9	0.057 (4)	0.047 (3)	0.0479 (14)	−0.013 (2)	−0.016 (3)	−0.001 (2)
C8A	0.034 (3)	0.034 (2)	0.0244 (8)	0.006 (2)	0.0007 (11)	−0.0152 (9)

C9A	0.057 (4)	0.047 (3)	0.0479 (14)	−0.013 (2)	−0.016 (3)	−0.001 (2)
C10	0.0157 (6)	0.0288 (7)	0.0149 (6)	0.0001 (5)	0.0037 (5)	0.0001 (5)
C11	0.0190 (6)	0.0261 (7)	0.0198 (6)	0.0005 (5)	0.0046 (5)	0.0000 (5)
C12	0.0190 (7)	0.0310 (8)	0.0228 (7)	−0.0046 (6)	0.0040 (5)	0.0004 (6)
C13	0.0149 (6)	0.0368 (8)	0.0179 (6)	0.0001 (6)	0.0038 (5)	0.0009 (6)
C14	0.0204 (7)	0.0296 (8)	0.0276 (7)	0.0037 (6)	0.0042 (5)	−0.0022 (6)
C15	0.0191 (7)	0.0265 (7)	0.0277 (7)	−0.0015 (6)	0.0041 (5)	−0.0026 (6)
C16	0.0171 (6)	0.0205 (7)	0.0194 (6)	−0.0012 (5)	0.0035 (5)	0.0018 (5)
C17	0.0181 (6)	0.0218 (7)	0.0200 (7)	−0.0016 (5)	0.0032 (5)	0.0020 (5)
C18	0.0210 (7)	0.0222 (7)	0.0207 (7)	−0.0012 (6)	0.0029 (5)	0.0019 (5)
C19	0.0287 (7)	0.0246 (7)	0.0194 (7)	−0.0010 (6)	0.0057 (5)	−0.0013 (6)
C20	0.0269 (7)	0.0347 (8)	0.0237 (7)	−0.0028 (6)	0.0036 (6)	−0.0027 (6)
C21	0.0357 (8)	0.0444 (10)	0.0213 (7)	−0.0037 (8)	0.0019 (6)	−0.0030 (7)
C22	0.0452 (9)	0.0420 (10)	0.0214 (7)	0.0009 (8)	0.0091 (7)	−0.0058 (7)
C23	0.0385 (9)	0.0406 (9)	0.0287 (8)	0.0103 (7)	0.0115 (7)	−0.0035 (7)
C24	0.0333 (8)	0.0337 (8)	0.0240 (7)	0.0079 (7)	0.0059 (6)	−0.0004 (6)

Geometric parameters (Å, º)

Cl1—C13	1.7433 (14)	C9—H9C	0.9800
S1—C17	1.7222 (14)	C8A—C9A	1.436 (4)
S1—C5	1.7511 (14)	C8A—H8C	0.9900
O1—C18	1.2196 (17)	C8A—H8D	0.9900
O2—C7	1.1989 (18)	C9A—H9D	0.9800
O3—C7	1.3284 (19)	C9A—H9E	0.9800
O3—C8A	1.473 (3)	C9A—H9F	0.9800
O3—C8	1.473 (3)	C10—C11	1.389 (2)
N1—C5	1.3320 (18)	C10—C15	1.393 (2)
N1—C1	1.3355 (18)	C11—C12	1.3939 (19)
N2—N3	1.2771 (17)	C11—H11	0.9500
N2—C16	1.3792 (17)	C12—C13	1.380 (2)
N3—N4	1.3792 (16)	C12—H12	0.9500
N4—C18	1.4140 (18)	C13—C14	1.386 (2)
N4—C19	1.4470 (17)	C14—C15	1.388 (2)
C1—C2	1.4131 (18)	C14—H14	0.9500
C1—C6	1.5028 (18)	C15—H15	0.9500
C2—C3	1.3902 (18)	C16—C17	1.3760 (19)
C2—C7	1.5035 (19)	C17—C18	1.4360 (19)
C3—C4	1.4094 (19)	C19—C24	1.388 (2)
C3—C10	1.4914 (18)	C19—C20	1.392 (2)
C4—C5	1.4040 (18)	C20—C21	1.389 (2)
C4—C16	1.4399 (18)	C20—H20	0.9500
C6—H6A	0.9800	C21—C22	1.384 (2)
C6—H6B	0.9800	C21—H21	0.9500
C6—H6C	0.9800	C22—C23	1.384 (2)
C8—C9	1.436 (3)	C22—H22	0.9500
C8—H8A	0.9900	C23—C24	1.387 (2)
C8—H8B	0.9900	C23—H23	0.9500

C9—H9A	0.9800	C24—H24	0.9500
C9—H9B	0.9800		

C17—S1—C5	89.68 (7)	C8A—C9A—H9D	109.5
C7—O3—C8A	113.2 (5)	C8A—C9A—H9E	109.5
C7—O3—C8	121.2 (3)	H9D—C9A—H9E	109.5
C5—N1—C1	116.19 (12)	C8A—C9A—H9F	109.5
N3—N2—C16	119.25 (12)	H9D—C9A—H9F	109.5
N2—N3—N4	121.09 (11)	H9E—C9A—H9F	109.5
N3—N4—C18	125.22 (11)	C11—C10—C15	119.49 (12)
N3—N4—C19	112.15 (11)	C11—C10—C3	121.48 (13)
C18—N4—C19	122.62 (11)	C15—C10—C3	119.03 (13)
N1—C1—C2	122.24 (12)	C10—C11—C12	120.44 (13)
N1—C1—C6	116.39 (12)	C10—C11—H11	119.8
C2—C1—C6	121.32 (13)	C12—C11—H11	119.8
C3—C2—C1	121.26 (13)	C13—C12—C11	118.95 (13)
C3—C2—C7	120.95 (12)	C13—C12—H12	120.5
C1—C2—C7	117.78 (12)	C11—C12—H12	120.5
C2—C3—C4	116.48 (12)	C12—C13—C14	121.68 (13)
C2—C3—C10	121.63 (12)	C12—C13—Cl1	119.16 (11)
C4—C3—C10	121.84 (12)	C14—C13—Cl1	119.16 (11)
C5—C4—C3	117.45 (12)	C13—C14—C15	118.82 (14)
C5—C4—C16	110.11 (12)	C13—C14—H14	120.6
C3—C4—C16	132.44 (12)	C15—C14—H14	120.6
N1—C5—C4	126.30 (13)	C14—C15—C10	120.60 (14)
N1—C5—S1	120.24 (10)	C14—C15—H15	119.7
C4—C5—S1	113.45 (10)	C10—C15—H15	119.7
C1—C6—H6A	109.5	C17—C16—N2	121.72 (13)
C1—C6—H6B	109.5	C17—C16—C4	112.46 (12)
H6A—C6—H6B	109.5	N2—C16—C4	125.74 (12)
C1—C6—H6C	109.5	C16—C17—C18	121.52 (12)
H6A—C6—H6C	109.5	C16—C17—S1	114.25 (11)
H6B—C6—H6C	109.5	C18—C17—S1	124.22 (10)
O2—C7—O3	125.50 (14)	O1—C18—N4	123.25 (13)
O2—C7—C2	124.66 (14)	O1—C18—C17	126.09 (13)
O3—C7—C2	109.83 (12)	N4—C18—C17	110.66 (12)
C9—C8—O3	109.1 (5)	C24—C19—C20	120.75 (13)
C9—C8—H8A	109.9	C24—C19—N4	118.50 (13)
O3—C8—H8A	109.9	C20—C19—N4	120.60 (13)
C9—C8—H8B	109.9	C21—C20—C19	118.92 (14)
O3—C8—H8B	109.9	C21—C20—H20	120.5
H8A—C8—H8B	108.3	C19—C20—H20	120.5
C8—C9—H9A	109.5	C22—C21—C20	120.86 (15)
C8—C9—H9B	109.5	C22—C21—H21	119.6
H9A—C9—H9B	109.5	C20—C21—H21	119.6
C8—C9—H9C	109.5	C23—C22—C21	119.44 (15)
H9A—C9—H9C	109.5	C23—C22—H22	120.3
H9B—C9—H9C	109.5	C21—C22—H22	120.3

C9A—C8A—O3	109.4 (7)	C22—C23—C24	120.78 (15)
C9A—C8A—H8C	109.8	C22—C23—H23	119.6
O3—C8A—H8C	109.8	C24—C23—H23	119.6
C9A—C8A—H8D	109.8	C23—C24—C19	119.23 (15)
O3—C8A—H8D	109.8	C23—C24—H24	120.4
H8C—C8A—H8D	108.2	C19—C24—H24	120.4
C16—N2—N3—N4	−3.7 (2)	C10—C11—C12—C13	−0.9 (2)
N2—N3—N4—C18	0.0 (2)	C11—C12—C13—C14	0.0 (2)
N2—N3—N4—C19	179.04 (13)	C11—C12—C13—Cl1	179.67 (10)
C5—N1—C1—C2	−0.5 (2)	C12—C13—C14—C15	1.2 (2)
C5—N1—C1—C6	−177.96 (13)	Cl1—C13—C14—C15	−178.50 (11)
N1—C1—C2—C3	−1.6 (2)	C13—C14—C15—C10	−1.5 (2)
C6—C1—C2—C3	175.69 (14)	C11—C10—C15—C14	0.6 (2)
N1—C1—C2—C7	179.53 (13)	C3—C10—C15—C14	−179.04 (13)
C6—C1—C2—C7	−3.1 (2)	N3—N2—C16—C17	1.0 (2)
C1—C2—C3—C4	3.2 (2)	N3—N2—C16—C4	−175.58 (13)
C7—C2—C3—C4	−178.00 (13)	C5—C4—C16—C17	−2.35 (17)
C1—C2—C3—C10	−174.38 (13)	C3—C4—C16—C17	177.86 (15)
C7—C2—C3—C10	4.4 (2)	C5—C4—C16—N2	174.47 (13)
C2—C3—C4—C5	−2.70 (19)	C3—C4—C16—N2	−5.3 (2)
C10—C3—C4—C5	174.87 (12)	N2—C16—C17—C18	5.6 (2)
C2—C3—C4—C16	177.08 (14)	C4—C16—C17—C18	−177.44 (13)
C10—C3—C4—C16	−5.3 (2)	N2—C16—C17—S1	−175.10 (11)
C1—N1—C5—C4	1.0 (2)	C4—C16—C17—S1	1.87 (16)
C1—N1—C5—S1	179.90 (10)	C5—S1—C17—C16	−0.66 (12)
C3—C4—C5—N1	0.7 (2)	C5—S1—C17—C18	178.62 (13)
C16—C4—C5—N1	−179.14 (13)	N3—N4—C18—O1	−174.77 (14)
C3—C4—C5—S1	−178.30 (10)	C19—N4—C18—O1	6.3 (2)
C16—C4—C5—S1	1.87 (15)	N3—N4—C18—C17	5.79 (19)
C17—S1—C5—N1	−179.80 (12)	C19—N4—C18—C17	−173.12 (13)
C17—S1—C5—C4	−0.75 (11)	C16—C17—C18—O1	172.31 (14)
C8A—O3—C7—O2	2.9 (6)	S1—C17—C18—O1	−6.9 (2)
C8—O3—C7—O2	−8.4 (4)	C16—C17—C18—N4	−8.27 (19)
C8A—O3—C7—C2	−178.4 (5)	S1—C17—C18—N4	172.50 (10)
C8—O3—C7—C2	170.3 (4)	N3—N4—C19—C24	28.53 (19)
C3—C2—C7—O2	−85.10 (19)	C18—N4—C19—C24	−152.44 (14)
C1—C2—C7—O2	93.74 (18)	N3—N4—C19—C20	−147.19 (14)
C3—C2—C7—O3	96.17 (16)	C18—N4—C19—C20	31.8 (2)
C1—C2—C7—O3	−84.98 (16)	C24—C19—C20—C21	−0.5 (2)
C7—O3—C8—C9	150.7 (4)	N4—C19—C20—C21	175.14 (15)
C7—O3—C8A—C9A	138.1 (7)	C19—C20—C21—C22	−0.7 (3)
C2—C3—C10—C11	−66.39 (18)	C20—C21—C22—C23	0.8 (3)
C4—C3—C10—C11	116.16 (15)	C21—C22—C23—C24	0.4 (3)
C2—C3—C10—C15	113.26 (16)	C22—C23—C24—C19	−1.6 (3)
C4—C3—C10—C15	−64.19 (18)	C20—C19—C24—C23	1.6 (2)
C15—C10—C11—C12	0.6 (2)	N4—C19—C24—C23	−174.09 (15)
C3—C10—C11—C12	−179.78 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O2^{i}	0.99	2.42	3.339 (7)	154

Symmetry code: (i) −*x*+1/2, *y*+1/2, −*z*+3/2.