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Diethyl 3-amino-6-methyl-4-[(*E*)-2-phenylethenyl]-thieno[2,3-*b*]pyridine-2,5-dicarboxylate

Joel T. Mague,[a] Shaaban K. Mohamed,[b,c] Mehmet Akkurt,[d] Etify A. Bakhite[e] and Mustafa R. Albayati[f]*

[a]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA, [b]Chemistry and Environmental Division, Manchester Metropolitan University, Manchester M1 5GD, England, [c]Chemistry Department, Faculty of Science, Minia University, 61519 El-Minia, Egypt, [d]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, [e]Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt, and [f]Kirkuk University, College of Science, Department of Chemistry, Kirkuk, Iraq. *Correspondence e-mail: shaabankamel@yahoo.com

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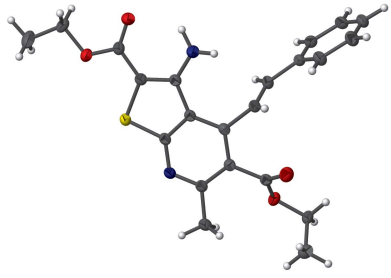
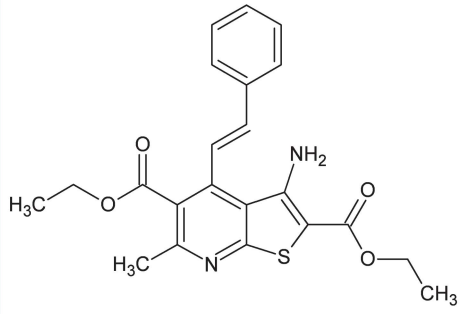
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{22}H_{22}N_2O_4S$, the bicyclic core is slightly folded [1.9 (1)°], while pairwise intermolecular N—H···O hydrogen bonding forms dimers across centers of symmetry. The dihedral angle between the phenyl ring an the six-membered ring of the bicyclic core is 75.50 (4)°. The molecular conformation is stabilized by an intramolecular N—H···O hydrogen bond with graph-set motif *S*(6) and by a weak C—H···O contact, forming an *S*(7) motif. In the crystal, π–π interactions [centroid-to-centroid distance = 3.7484 (10) Å] between phenyl rings and two weak C—H···π interactions are also observed.

3D view



Chemical scheme



Structure description

In organic chemistry, pyridine derivatives have received considerable attention due to their diverse biological activities such as anti-inflammatory and analgesic agents (Hill, 2010; Kumar *et al.*, 2010). The synthesis of different thienopyridines and their biological applications have been the subject of several articles which demonstrate the high importance of this class of compounds (Ho & Wang, 1995; Bakhite, 2003; Litvinov *et al.*, 2005). In this context, we here report the synthesis and crystal structure of the title compound.

The dihedral angle between the phenyl ring (C1–C6) and the six-membered ring of the bicyclic core is 75.50 (4)° while that between the five- and six-membered rings in the bicyclic core is 1.9 (1)°. The conformation of the carboxyethyl substituent on the five-membered ring is partially determined by the intramolecular N2—H2*B*···O3 hydrogen bond with graph-set motif *S*(6) (Table 1 and Fig. 1). The same H atom also participates in

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

*Cg*1 and *Cg*2 are the centroids of the C1–C6 phenyl ring and the N1/C9–C13 pyridine ring, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O3	0.92 (2)	2.15 (2)	2.796 (2)	127.0 (18)
N2—H2*B*···O3^{i}	0.92 (2)	2.20 (2)	2.966 (2)	140.2 (19)
C19—H19*B*···*Cg*1^{i}	0.98	2.95	3.766 (2)	141
C22—H22*A*···*Cg*2^{ii}	0.98	2.95	3.9206 (19)	170
C7—H7···O1^{iii}	0.95	2.46	3.352 (2)	157

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $x+1, y, z$.

a pairwise, intermolecular hydrogen-bonding interaction N2—H2*B*···O3^{i} [symmetry code: (i) $-x+2, -y+1, -z+1$], which forms dimers with $R_2^2(12)$ motifs (Fig. 2 and Table 1). The weak C7—H7···O1 contact further stabilizes the molecular conformation, forming an $S(7)$ motif. In addition, the π–π interaction [centroid-to-centroid distance = 3.7484 (10) Å] between the C1–C6 phenyl rings, and two weak C—H···π interactions help to consolidate the packing.

Synthesis and crystallization

To a mixture of ethyl 3-cyano-1,2-dihydro-6-methyl-4-(2-phenylethenyl)-2-thioxopyridine-5-χarboxylate (10 mmol) and ethyl chloroacetate (10 mmol) in absolute ethanol (30 ml), anhydrous sodium carbonate (3.2 g) was added. The reaction mixture was heated under reflux for 3 h. Sodium carbonate was filtered off while hot and the clear filtrate was allowed to cool. The solid that formed was collected by filtration, washed several times with water and recrystallized from ethanol solution to give the title compound in the form of yellow crystals. Yield (78%); m.p. 389–390 K; IR (KBr) ν = 3491, 3349 (NH_2), 1714 (C═O, ester group at C-5), 1671 (C═O, ester group at C-2) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.74–7.78 (*d*, *J* =16 Hz, 1H, ethene proton), 7.64–7.66 (*d*, *J* =8 Hz, 2H, ArH), 7.37–7.43 (*m*, 3H, ArH), 6.78–6.82 (*d*, *J* =16 Hz, 1H, ethene proton), 6.61(*s*, 2H, NH_2), 4.24–4.27 (*m*, 4H, two OCH_2 groups), 2.57 (*s*, 3H, CH_3 at C-6), 1.28–1.29 (*t*, 3H, CH_3 of ester group), 1.15–1.16 (*t*, 3H, CH_3 of ester group) p.p.m.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{22}N_2O_4S$
M_r	410.47
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, *b*, *c* (Å)	5.6473 (2), 26.7798 (9), 13.3219 (4)
β (°)	99.743 (2)
V (Å^3)	1985.66 (11)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	1.72
Crystal size (mm)	0.20 × 0.08 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.81, 0.93
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14981, 3830, 3158
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.094, 1.07
No. of reflections	3830
No. of parameters	273
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.31

Computer programs: *APEX2* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012), *SHELXTL* (Sheldrick, 2008).

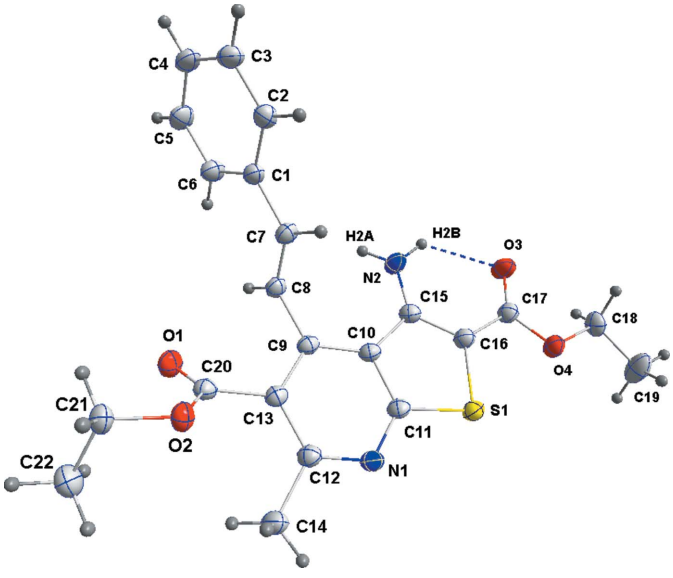


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids. The intramolecular N—H···O bond is shown as a dotted line.

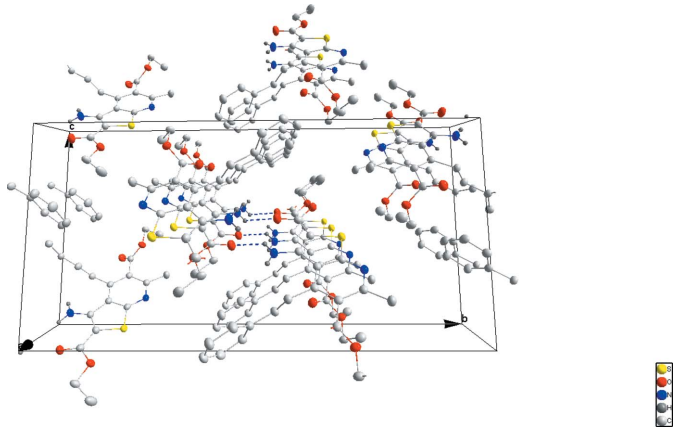


Figure 2
Packing viewed down the *a* axis. Intermolecular N—H···O hydrogen bonds are shown as dotted lines.

Refinement

H-atoms 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 carbon atoms. Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160270 [https://doi.org/10.1107/S2414314616002704]

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Crystal data

$C_{22}H_{22}N_2O_4S$
M_r = 410.47
Monoclinic, $P2_1/n$
a = 5.6473 (2) Å
b = 26.7798 (9) Å
c = 13.3219 (4) Å
β = 99.743 (2)°
V = 1985.66 (11) Å^3
Z = 4
$F(000)$ = 864
D_x = 1.373 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9033 reflections
θ = 3.3–72.0°
μ = 1.72 mm^{-1}
T = 150 K
Column, yellow
0.20 × 0.08 × 0.05 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, 2015)
T_{min} = 0.81, T_{max} = 0.93
14981 measured reflections
3830 independent reflections
3158 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 72.0°, θ_{min} = 3.3°
h = −6→6
k = −33→31
l = −16→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.07
3830 reflections
273 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
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.6171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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 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 carbon atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.81665 (7)	0.31695 (2)	0.51587 (3)	0.02555 (12)
O1	−0.0116 (2)	0.37752 (4)	0.80094 (9)	0.0313 (3)
O2	0.1931 (2)	0.31306 (4)	0.88190 (9)	0.0261 (3)
O3	1.0260 (3)	0.45058 (5)	0.44348 (11)	0.0373 (3)
O4	1.1080 (2)	0.37241 (4)	0.39666 (9)	0.0292 (3)
N1	0.5078 (2)	0.28245 (5)	0.63005 (10)	0.0247 (3)
N2	0.6910 (3)	0.45759 (5)	0.57515 (13)	0.0316 (3)
H2A	0.601 (4)	0.4709 (8)	0.6114 (17)	0.039 (6)*
H2B	0.789 (4)	0.4766 (8)	0.5425 (17)	0.043 (6)*
C1	0.4979 (3)	0.50473 (6)	0.84071 (12)	0.0232 (3)
C2	0.6874 (3)	0.52120 (6)	0.91401 (13)	0.0257 (3)
H2	0.8334	0.5028	0.9252	0.031*
C3	0.6674 (3)	0.56382 (6)	0.97084 (13)	0.0301 (4)
H3	0.7980	0.5742	1.0211	0.036*
C4	0.4573 (3)	0.59124 (6)	0.95430 (14)	0.0313 (4)
H4	0.4420	0.6203	0.9937	0.038*
C5	0.2685 (3)	0.57614 (7)	0.87975 (14)	0.0328 (4)
H5	0.1250	0.5953	0.8672	0.039*
C6	0.2883 (3)	0.53313 (6)	0.82343 (13)	0.0290 (4)
H6	0.1580	0.5230	0.7728	0.035*
C7	0.5254 (3)	0.45678 (6)	0.79016 (12)	0.0241 (3)
H7	0.6806	0.4421	0.8031	0.029*
C8	0.3566 (3)	0.43171 (6)	0.72829 (12)	0.0226 (3)
H8	0.2029	0.4464	0.7081	0.027*
C9	0.4041 (3)	0.38108 (6)	0.69013 (12)	0.0211 (3)
C10	0.5636 (3)	0.37290 (6)	0.62112 (12)	0.0217 (3)
C11	0.6091 (3)	0.32310 (6)	0.59683 (12)	0.0226 (3)
C12	0.3520 (3)	0.29013 (6)	0.69361 (12)	0.0240 (3)
C13	0.3009 (3)	0.33872 (6)	0.72724 (12)	0.0217 (3)

C14	0.2322 (3)	0.24380 (6)	0.72435 (14)	0.0322 (4)
H14A	0.2435	0.2172	0.6749	0.048*
H14B	0.0627	0.2509	0.7262	0.048*
H14C	0.3122	0.2331	0.7920	0.048*
C15	0.7021 (3)	0.40730 (6)	0.56948 (12)	0.0228 (3)
C16	0.8451 (3)	0.38195 (6)	0.51149 (12)	0.0242 (3)
C17	0.9986 (3)	0.40561 (6)	0.44930 (13)	0.0255 (3)
C18	1.2648 (3)	0.39335 (7)	0.33177 (13)	0.0296 (4)
H18A	1.4040	0.4101	0.3735	0.035*
H18B	1.1768	0.4182	0.2845	0.035*
C19	1.3474 (4)	0.35096 (8)	0.27367 (17)	0.0456 (5)
H19A	1.4366	0.3270	0.3213	0.068*
H19B	1.4520	0.3637	0.2278	0.068*
H19C	1.2077	0.3344	0.2337	0.068*
C20	0.1416 (3)	0.34570 (6)	0.80479 (12)	0.0227 (3)
C21	0.0355 (3)	0.31326 (7)	0.95820 (13)	0.0282 (4)
H21A	−0.0058	0.3481	0.9729	0.034*
H21B	0.1207	0.2983	1.0221	0.034*
C22	−0.1910 (3)	0.28440 (7)	0.92170 (14)	0.0335 (4)
H22A	−0.2796	0.3003	0.8604	0.050*
H22B	−0.2910	0.2841	0.9751	0.050*
H22C	−0.1500	0.2501	0.9059	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0313 (2)	0.0205 (2)	0.0267 (2)	−0.00010 (16)	0.01026 (16)	−0.00271 (15)
O1	0.0305 (6)	0.0294 (6)	0.0352 (7)	0.0074 (5)	0.0091 (5)	0.0038 (5)
O2	0.0267 (6)	0.0294 (6)	0.0234 (6)	0.0038 (5)	0.0078 (5)	0.0039 (5)
O3	0.0499 (8)	0.0242 (6)	0.0433 (8)	−0.0061 (6)	0.0234 (6)	−0.0035 (5)
O4	0.0342 (6)	0.0266 (6)	0.0300 (7)	0.0010 (5)	0.0151 (5)	0.0008 (5)
N1	0.0309 (7)	0.0197 (6)	0.0242 (7)	−0.0020 (6)	0.0066 (6)	−0.0013 (5)
N2	0.0428 (9)	0.0197 (7)	0.0369 (9)	0.0000 (7)	0.0194 (7)	0.0002 (6)
C1	0.0262 (8)	0.0209 (7)	0.0232 (8)	−0.0020 (6)	0.0062 (6)	−0.0023 (6)
C2	0.0244 (8)	0.0262 (8)	0.0262 (9)	−0.0017 (7)	0.0038 (6)	−0.0006 (7)
C3	0.0354 (9)	0.0279 (9)	0.0268 (9)	−0.0078 (7)	0.0044 (7)	−0.0052 (7)
C4	0.0412 (10)	0.0236 (8)	0.0308 (9)	−0.0039 (7)	0.0112 (8)	−0.0071 (7)
C5	0.0341 (9)	0.0264 (9)	0.0385 (10)	0.0047 (7)	0.0079 (8)	−0.0047 (8)
C6	0.0288 (9)	0.0259 (8)	0.0314 (9)	0.0014 (7)	0.0024 (7)	−0.0045 (7)
C7	0.0250 (8)	0.0221 (8)	0.0253 (8)	0.0034 (6)	0.0046 (6)	−0.0025 (6)
C8	0.0238 (8)	0.0199 (8)	0.0246 (8)	0.0026 (6)	0.0051 (6)	−0.0009 (6)
C9	0.0215 (7)	0.0206 (7)	0.0201 (8)	0.0001 (6)	0.0003 (6)	−0.0022 (6)
C10	0.0238 (8)	0.0204 (7)	0.0203 (8)	−0.0006 (6)	0.0020 (6)	−0.0015 (6)
C11	0.0257 (8)	0.0217 (8)	0.0197 (8)	−0.0011 (6)	0.0018 (6)	−0.0025 (6)
C12	0.0284 (8)	0.0222 (8)	0.0212 (8)	−0.0013 (6)	0.0039 (6)	−0.0006 (6)
C13	0.0226 (8)	0.0221 (8)	0.0196 (8)	0.0004 (6)	0.0015 (6)	−0.0008 (6)
C14	0.0439 (10)	0.0219 (8)	0.0336 (10)	−0.0047 (7)	0.0144 (8)	−0.0021 (7)
C15	0.0250 (8)	0.0209 (8)	0.0220 (8)	−0.0012 (6)	0.0029 (6)	−0.0010 (6)

C16	0.0274 (8)	0.0216 (8)	0.0239 (8)	−0.0006 (6)	0.0055 (6)	−0.0002 (6)
C17	0.0282 (8)	0.0265 (8)	0.0226 (8)	0.0001 (7)	0.0061 (6)	−0.0021 (6)
C18	0.0299 (9)	0.0351 (9)	0.0259 (9)	0.0013 (7)	0.0110 (7)	0.0059 (7)
C19	0.0599 (13)	0.0407 (11)	0.0437 (12)	0.0131 (10)	0.0299 (10)	0.0083 (9)
C20	0.0239 (8)	0.0217 (7)	0.0219 (8)	−0.0019 (6)	0.0024 (6)	−0.0012 (6)
C21	0.0339 (9)	0.0303 (9)	0.0228 (8)	−0.0013 (7)	0.0114 (7)	−0.0001 (7)
C22	0.0303 (9)	0.0374 (10)	0.0336 (10)	−0.0015 (8)	0.0076 (7)	0.0029 (8)

Geometric parameters (Å, º)

S1—C11	1.7297 (17)	C8—C9	1.488 (2)
S1—C16	1.7498 (16)	C8—H8	0.9500
O1—C20	1.209 (2)	C9—C13	1.403 (2)
O2—C20	1.3428 (19)	C9—C10	1.409 (2)
O2—C21	1.4601 (19)	C10—C11	1.406 (2)
O3—C17	1.218 (2)	C10—C15	1.455 (2)
O4—C17	1.346 (2)	C12—C13	1.421 (2)
O4—C18	1.451 (2)	C12—C14	1.503 (2)
N1—C12	1.336 (2)	C13—C20	1.492 (2)
N1—C11	1.339 (2)	C14—H14A	0.9800
N2—C15	1.351 (2)	C14—H14B	0.9800
N2—H2A	0.84 (2)	C14—H14C	0.9800
N2—H2B	0.92 (2)	C15—C16	1.386 (2)
C1—C6	1.393 (2)	C16—C17	1.443 (2)
C1—C2	1.393 (2)	C18—C19	1.492 (3)
C1—C7	1.470 (2)	C18—H18A	0.9900
C2—C3	1.385 (2)	C18—H18B	0.9900
C2—H2	0.9500	C19—H19A	0.9800
C3—C4	1.381 (3)	C19—H19B	0.9800
C3—H3	0.9500	C19—H19C	0.9800
C4—C5	1.389 (3)	C21—C22	1.503 (2)
C4—H4	0.9500	C21—H21A	0.9900
C5—C6	1.389 (2)	C21—H21B	0.9900
C5—H5	0.9500	C22—H22A	0.9800
C6—H6	0.9500	C22—H22B	0.9800
C7—C8	1.331 (2)	C22—H22C	0.9800
C7—H7	0.9500		
C11—S1—C16	90.11 (8)	C9—C13—C20	118.53 (14)
C20—O2—C21	116.82 (13)	C12—C13—C20	120.75 (14)
C17—O4—C18	115.82 (13)	C12—C14—H14A	109.5
C12—N1—C11	116.63 (14)	C12—C14—H14B	109.5
C15—N2—H2A	119.6 (15)	H14A—C14—H14B	109.5
C15—N2—H2B	119.4 (14)	C12—C14—H14C	109.5
H2A—N2—H2B	121 (2)	H14A—C14—H14C	109.5
C6—C1—C2	118.27 (15)	H14B—C14—H14C	109.5
C6—C1—C7	123.63 (15)	N2—C15—C16	123.83 (16)
C2—C1—C7	118.00 (15)	N2—C15—C10	124.82 (15)

C3—C2—C1	121.34 (16)	C16—C15—C10	111.34 (14)
C3—C2—H2	119.3	C15—C16—C17	124.61 (15)
C1—C2—H2	119.3	C15—C16—S1	113.78 (12)
C4—C3—C2	119.90 (16)	C17—C16—S1	121.57 (12)
C4—C3—H3	120.1	O3—C17—O4	123.05 (16)
C2—C3—H3	120.1	O3—C17—C16	124.46 (16)
C3—C4—C5	119.62 (16)	O4—C17—C16	112.48 (14)
C3—C4—H4	120.2	O4—C18—C19	106.91 (15)
C5—C4—H4	120.2	O4—C18—H18A	110.3
C4—C5—C6	120.36 (17)	C19—C18—H18A	110.3
C4—C5—H5	119.8	O4—C18—H18B	110.3
C6—C5—H5	119.8	C19—C18—H18B	110.3
C5—C6—C1	120.48 (16)	H18A—C18—H18B	108.6
C5—C6—H6	119.8	C18—C19—H19A	109.5
C1—C6—H6	119.8	C18—C19—H19B	109.5
C8—C7—C1	127.15 (15)	H19A—C19—H19B	109.5
C8—C7—H7	116.4	C18—C19—H19C	109.5
C1—C7—H7	116.4	H19A—C19—H19C	109.5
C7—C8—C9	121.31 (14)	H19B—C19—H19C	109.5
C7—C8—H8	119.3	O1—C20—O2	123.53 (15)
C9—C8—H8	119.3	O1—C20—C13	124.74 (15)
C13—C9—C10	116.98 (14)	O2—C20—C13	111.70 (13)
C13—C9—C8	120.46 (14)	O2—C21—C22	111.01 (14)
C10—C9—C8	122.44 (14)	O2—C21—H21A	109.4
C11—C10—C9	117.36 (14)	C22—C21—H21A	109.4
C11—C10—C15	110.97 (14)	O2—C21—H21B	109.4
C9—C10—C15	131.64 (14)	C22—C21—H21B	109.4
N1—C11—C10	126.14 (15)	H21A—C21—H21B	108.0
N1—C11—S1	120.07 (12)	C21—C22—H22A	109.5
C10—C11—S1	113.79 (12)	C21—C22—H22B	109.5
N1—C12—C13	122.07 (15)	H22A—C22—H22B	109.5
N1—C12—C14	114.88 (14)	C21—C22—H22C	109.5
C13—C12—C14	123.03 (15)	H22A—C22—H22C	109.5
C9—C13—C12	120.71 (15)	H22B—C22—H22C	109.5

C6—C1—C2—C3	1.9 (3)	C8—C9—C13—C20	0.6 (2)
C7—C1—C2—C3	−174.57 (16)	N1—C12—C13—C9	3.5 (2)
C1—C2—C3—C4	−0.9 (3)	C14—C12—C13—C9	−175.08 (15)
C2—C3—C4—C5	−0.8 (3)	N1—C12—C13—C20	−174.94 (14)
C3—C4—C5—C6	1.4 (3)	C14—C12—C13—C20	6.5 (2)
C4—C5—C6—C1	−0.2 (3)	C11—C10—C15—N2	177.80 (16)
C2—C1—C6—C5	−1.4 (3)	C9—C10—C15—N2	−4.0 (3)
C7—C1—C6—C5	174.92 (17)	C11—C10—C15—C16	−1.02 (19)
C6—C1—C7—C8	−5.4 (3)	C9—C10—C15—C16	177.15 (16)
C2—C1—C7—C8	170.89 (17)	N2—C15—C16—C17	−0.5 (3)
C1—C7—C8—C9	−174.13 (16)	C10—C15—C16—C17	178.33 (15)
C7—C8—C9—C13	107.59 (19)	N2—C15—C16—S1	−178.27 (14)
C7—C8—C9—C10	−68.3 (2)	C10—C15—C16—S1	0.57 (18)

C13—C9—C10—C11	−1.1 (2)	C11—S1—C16—C15	0.02 (13)
C8—C9—C10—C11	174.93 (14)	C11—S1—C16—C17	−177.82 (14)
C13—C9—C10—C15	−179.21 (15)	C18—O4—C17—O3	0.4 (2)
C8—C9—C10—C15	−3.1 (3)	C18—O4—C17—C16	179.71 (13)
C12—N1—C11—C10	−1.2 (2)	C15—C16—C17—O3	2.6 (3)
C12—N1—C11—S1	178.99 (12)	S1—C16—C17—O3	−179.77 (15)
C9—C10—C11—N1	2.8 (2)	C15—C16—C17—O4	−176.65 (15)
C15—C10—C11—N1	−178.75 (15)	S1—C16—C17—O4	0.9 (2)
C9—C10—C11—S1	−177.40 (11)	C17—O4—C18—C19	−174.66 (15)
C15—C10—C11—S1	1.06 (17)	C21—O2—C20—O1	7.0 (2)
C16—S1—C11—N1	179.19 (14)	C21—O2—C20—C13	−174.78 (13)
C16—S1—C11—C10	−0.63 (13)	C9—C13—C20—O1	43.9 (2)
C11—N1—C12—C13	−1.9 (2)	C12—C13—C20—O1	−137.68 (17)
C11—N1—C12—C14	176.71 (14)	C9—C13—C20—O2	−134.31 (14)
C10—C9—C13—C12	−1.7 (2)	C12—C13—C20—O2	44.1 (2)
C8—C9—C13—C12	−177.87 (14)	C20—O2—C21—C22	80.53 (18)
C10—C9—C13—C20	176.70 (13)		

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the C1–C6 phenyl ring and the N1/C9–C13 pyridine ring, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O3	0.92 (2)	2.15 (2)	2.796 (2)	127.0 (18)
N2—H2*B*···O3^{i}	0.92 (2)	2.20 (2)	2.966 (2)	140.2 (19)
C19—H19*B*···*Cg*1^{i}	0.98	2.95	3.766 (2)	141
C22—H22*A*···*Cg*2^{ii}	0.98	2.95	3.9206 (19)	170
C7—H7···O1^{iii}	0.95	2.46	3.352 (2)	157

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