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Crystal structures of ethyl {2-[4-(4-isopropylphenyl)thiazol-2-yl]phenyl}carbamate and ethyl {2-[4-(3-nitrophenyl)thiazol-2-yl]phenyl}carbamate

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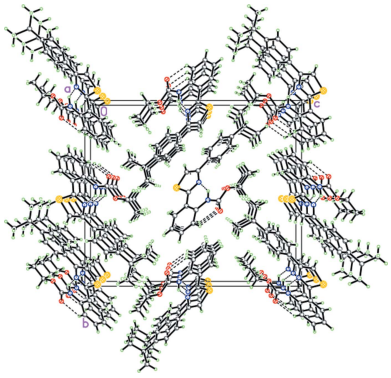
Supporting information: this article has supporting information at journals.iucr.org/e

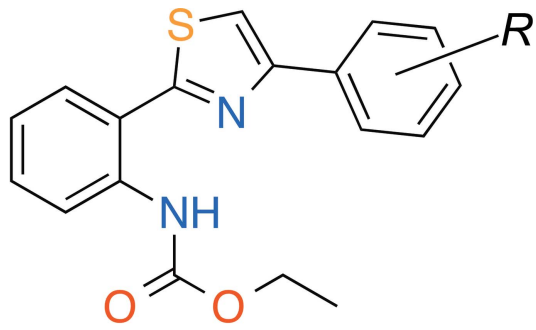
The title compounds, $C_{21}H_{22}N_2O_2S$ (I) and $C_{18}H_{15}N_3O_4S$ (II), are structural analogs of the alkaloid Thiosporine B. Both molecules adopt a near-planar V-shaped conformation, which is consolidated by intramolecular N—H···N and C—H···O hydrogen bonds. The crystal structure of (I) consists of mlecular stacks along the *a* axis, in which the molecules are linked to each other by π(S)···π(C) interactions. In the crystal of (II), molecules are linked into chains by C—H···O hydrogen bonds and the chains are cross-linked into (100) sheets by π–π stacking interactions.

1. Chemical context

Marine actinomycetes are prolific producers of biologically active natural products. This unique habitat has led to the abundant chemical diversity of metabolites that provides a foundation for the discovery of promising drug lead compounds. Among all known marine microbial secondary metabolites, over half were produced by actinomycetes (Fenical & Jensen, 2006; Lam *et al.*, 2006; Fu *et al.*, 2011). From this resource, more than 400 new active secondary metabolites have been isolated (Bérdy, 2005; Bull & Stach, 2007; Molinski *et al.*, 2009). Some of them represented by abyssomycin C (Bister *et al.*, 2004), diazepinomicin (Charan *et al.*, 2004), salinosporamide A (Feling *et al.*, 2003) and the marinomycins (Kwon *et al.*, 2006) are potent antibiotics and possess novel structures. A comparatively large class of natural compounds possessing biological activity contains imidazole, thiazole, or oxazole moieties. Studies of biological activity (Zabriskie *et al.*, 1990; Carroll *et al.*, 1996; Taori *et al.*, 2008) as well as a total synthesis of thiazoles containing alkaloids isolated from marine microorganisms are very important directions. In many cases, the substances mentioned above have promising anti-tumor (Luesch *et al.*, 2001) and antibacterial (Shimanaka *et al.*, 1994; Yun *et al.*, 1994) activities.

In this paper we report a synthetic approach to the preparation of new thiazole derivatives (I) and (II) containing aryl fragments – the structural analogs of alkaloid Thiosporine B (Fu & MacMillan, 2015) – and their investigation by single crystal X-ray diffraction.





(I) R = 4-i-Pr
(II) R = 3-NO_2

2. Structural commentary

Compounds (I), $C_{21}H_{22}N_2O_2S$, and (II), $C_{18}H_{15}N_3O_4S$, have very similar molecular geometries (Figs. 1 and 2), allowing for the different substituents on the benzene rings. Both molecules adopt a near-planar V-shaped conformation, which is consolidated by intramolecular N7—H7···N3 and C8—H8···O1 hydrogen bonds (Tables 1 and 2, Figs. 1 and 2) as well as an intermolecular π–π interactions (see Section 3 below). There exists a small twist of 10.27 (15)° between the central thiazole and 4-benzene rings in (I) only. Surprisingly, the ethyl (phenyl)carbamate substituents (with the exception of some hydrogen atoms of the ethyl fragment) are perfectly coplanar with the thiazole ring in both molecules.

The bond-length distributions within the thiazole rings of (I) and (II) are almost identical, clearly indicating that some degree of delocalization is present. These values are in good agreement with those observed in related structures (Garden *et al.*, 2007; Sen *et al.*, 2013; Bunev *et al.*, 2014; Mague *et al.*, 2014; Moreno-Fuquen *et al.*, 2015; AaminaNaaz *et al.*, 2015). The C—S—C angle in (I) [89.70 (12)°] and (II) [89.94 (12)°] is also very close to that in the previously reported analogous structures [89.0 (2)–90.3 (5)°; Nayak *et al.*, 2009; Hua *et al.*, 2014).

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

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7···N3	0.97 (2)	1.84 (2)	2.682 (3)	144 (2)
C8—H8···O1	0.95	2.32	2.954 (3)	124

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^{i}	0.95	2.32	3.260 (3)	168
N7—H7···N3	0.80 (3)	1.98 (3)	2.672 (3)	144 (3)
C8—H8···O1	0.95	2.32	2.946 (3)	123

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

3. Supramolecular features

Although the similarity of the molecular geometries and types of intramolecular interactions might lead to similar packing motifs, this is not found in the case of (I) and (II). The intermolecular interactions, namely, π–π interactions and C—H···O hydrogen bonding, combined in a different way, give rise to various packing networks.

In (I), the crystal packing consists of stacks along the a axis (Fig. 3), in which the molecules are linked to each other by π(S1)···π(C7) [1 + x, y, z] interactions at distances of 3.463 (3) Å (Fig. 4). No other directional intermolecular interactions are observed in (I).

The situation in the case of (II) is quite different. The molecules of (II) form chains *via* C5—H5···O1($-x+\frac{3}{2}, y-1, z-\frac{1}{2}$) hydrogen bonds (Table 1, Fig. 5). It should be pointed

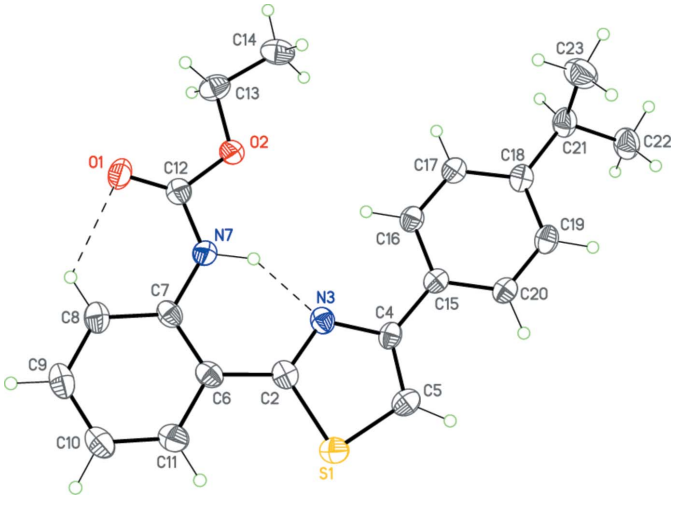


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate the intramolecular hydrogen bonds. H atoms are presented as small spheres of arbitrary radius.

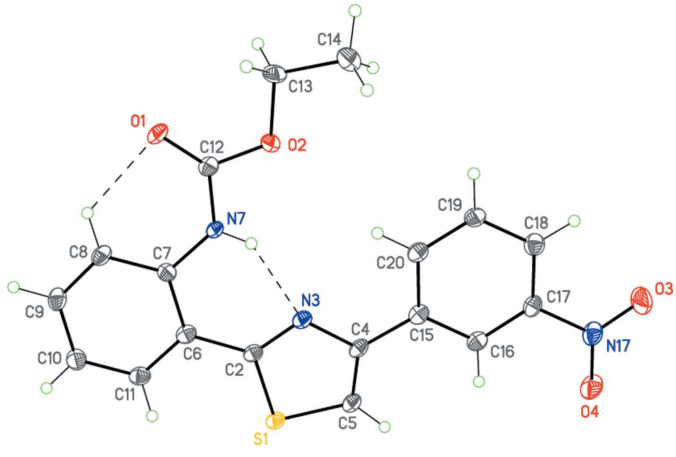


Figure 2
The molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate the intramolecular hydrogen bonds. H atoms are presented as small spheres of arbitrary radius.

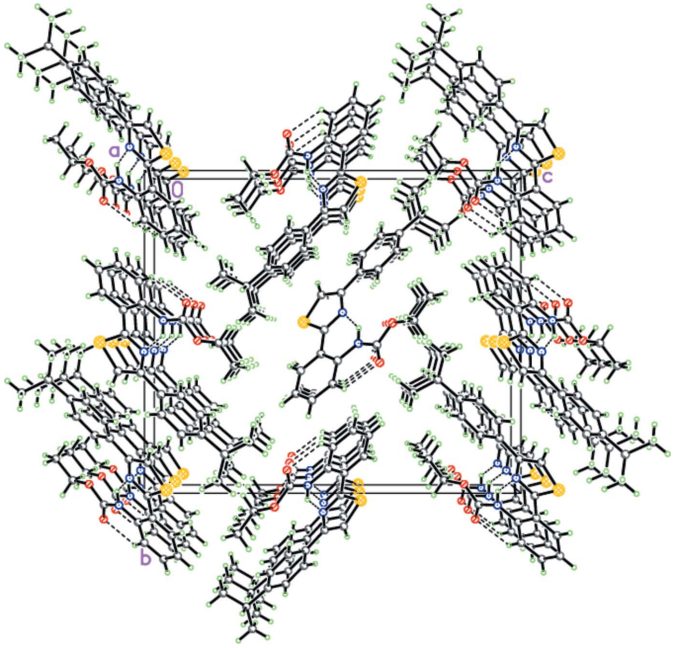


Figure 3
The crystal structure of (I). Dashed lines indicate the intramolecular N—H···N and C—H···O hydrogen bonds.

out that the molecules within the chains are coplanar, forming a ribbon-like motif. Further, the ribbons are packed in layers parallel to (100) *via* π–π stacking interactions (Fig. 6). The distance between the ribbons in the layers is 3.216 (3) Å. Importantly, the ribbons of adjacent layers are not parallel to each other, but disposed at an interplane angle of 39.91 (2)° (Fig. 6). Thus, the crystal of (II) comprises alternating layers, in which molecules are arranged in a different manner.

4. Synthesis and crystallization

A solution of ethyl (2-carbamothioylphenyl)carbamate (2.24 g, 10 mmol) and the appropriately substituted phenacyl bromide (10 mmol) in 95% EtOH (50 ml) was heated for 12 h under reflux. After cooling to room temperature, the solution

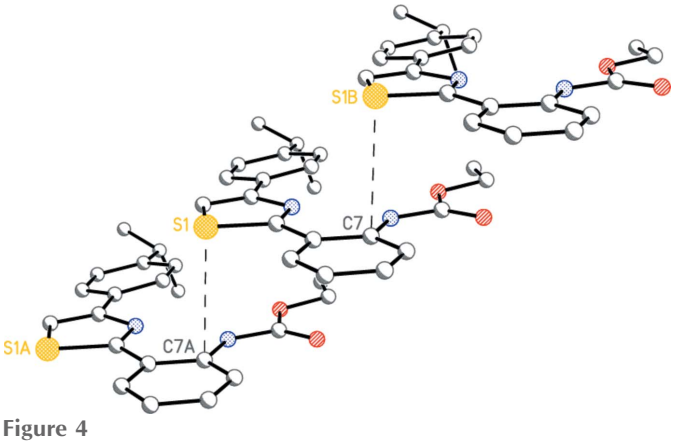


Figure 4
A fragment of the stack in (I). Dashed lines indicate the intermolecular S···C interactions within the stack.

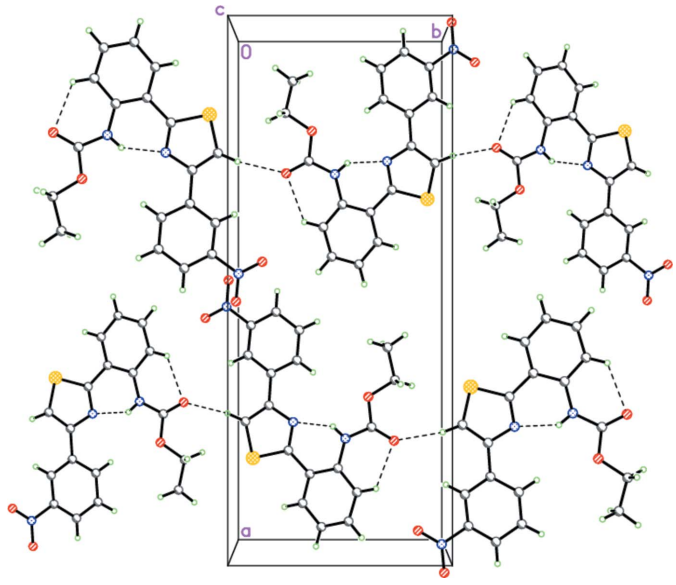


Figure 5
The hydrogen-bonded chains of (II). Dashed lines indicate the intramolecular N—H···N and C—H···O and intermolecular C—H···O hydrogen bonds.

was basified with saturated $NaHCO_3$ solution to yield the expected product (I) or (II) (Fig. 7). The reaction mixture was filtered and the isolated solid was washed with water and dried

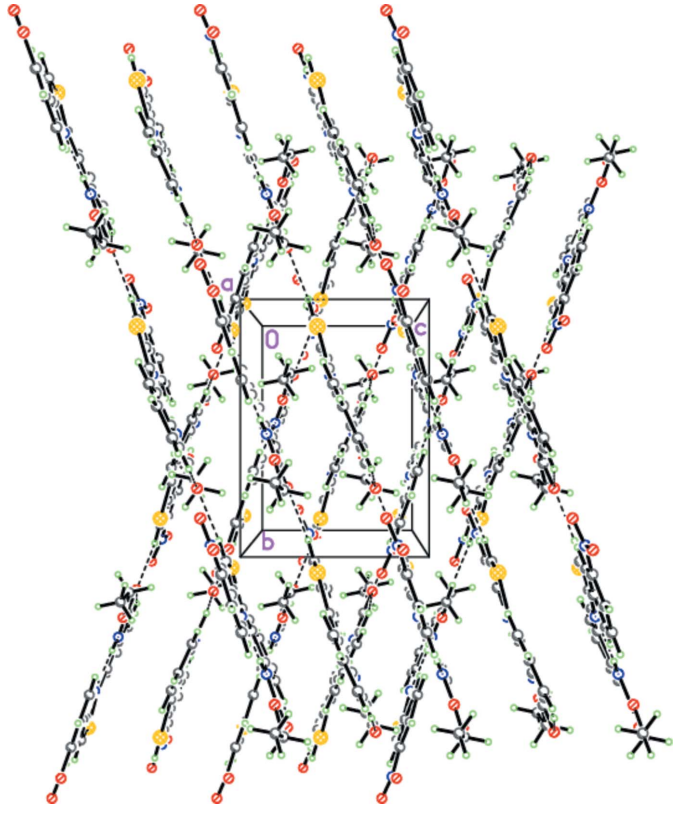


Figure 6
Crystal structure of (II) demonstrating the mutual arrangement of the hydrogen-bonded chains. Dashed lines indicate the intramolecular N—H···N and C—H···O and intermolecular C—H···O hydrogen bonds.

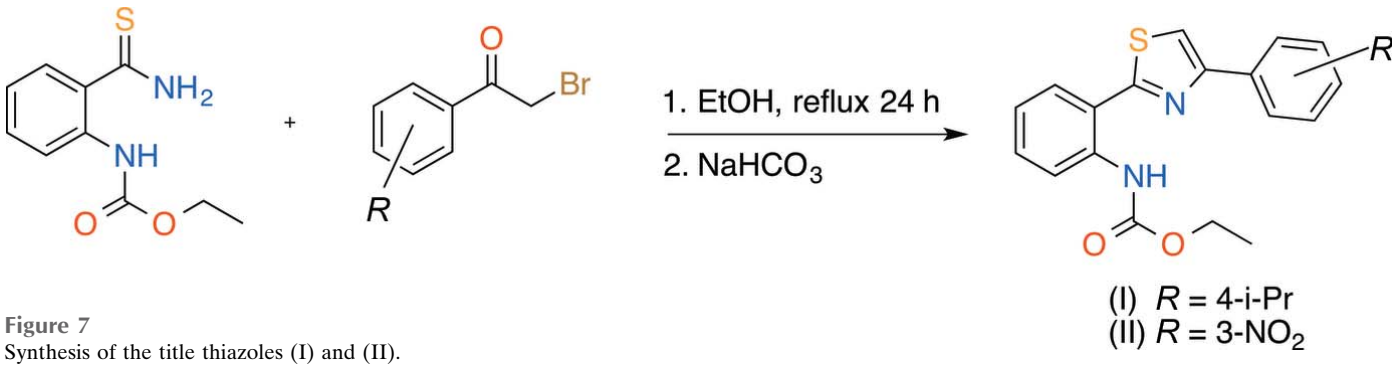


Figure 7
Synthesis of the title thiazoles (I) and (II).

in vacuo. The compounds were isolated as pale-yellow crystalline solids in 51% and 74% yield for the *i*-propyl (I) and nitro (II) derivatives, respectively. Single crystals of the products were obtained by slow crystallization from *N*,*N*-dimethylformamide solution.

Spectroscopic and physical data for (I): M.p. 379-381 K. FT–IR (ν_{max}, cm^{-1}): 3090, 1982, 1725, 1603, 1544, 1487, 1312, 1240, 1071. ^{1}H NMR (600 MHz, DMSO-d_6, 304 K): δ = 1.25 (*d*, 6H, *J* = 6.9), 1.33 (*t*, 3H, *J* = 7.1), 2.96 (*h*, 1H, *J* = 7.2), 4.21 (*q*, 2H, *J* = 7.1), 7.19 (*t*, 1H, *J* = 7.6), 7.37 (*d*, 2H, *J* = 8.2), 7.50 (*t*, 1H, *J* = 7.8), 7.92 (*d*, 1H, *J* = 7.8), 7.96 (*d*, 2H, *J* = 8.1), 8.20 (*s*, 1H), 8.29 (*d*, 1H, *J* = 8.3), 12.02 (*s*, 1H). Analysis calculated for $C_{21}H_{22}N_2O_2S$: C, 68.83; H, 6.05; N, 7.64. Found: C, 68.88; H, 5.99; N, 7.67.

Spectroscopic and physical data for (II): M.p. 478–479 K. FT–IR (ν_{max}, cm^{-1}): 3090, 1720, 1600, 1545, 1483, 1352, 1244, 1071. ^{1}H NMR (600 MHz, DMSO-d_6, 304 K): δ = 1.31 (*t*, 3H, *J* = 7.1), 4.23 (*q*, 2H, *J* = 7.1), 7.23 (*t*, 1H, *J* = 8.0), 7.49–7.64 (*m*, 1H), 7.83 (*t*, 1H, *J* = 8.0), 7.99 (*d*, 1H, *J* = 7.9), 8.28 (*d*, 1H, *J* = 7.5), 8.48 (*d*, 1H, *J* = 7.9), 8.85 (*s*, 1H), 11.65 (*s*, 1H). Analysis calculated for $C_{18}H_{15}N_3O_4S$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.59; H, 4.13; N, 11.47.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. X-ray diffraction studies were carried out on the 'Belok' beamline (λ = 0.96990 Å) of the

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{21}H_{22}N_2O_2S$	$C_{18}H_{15}N_3O_4S$
M_r	366.47	369.39
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $Pca2_1$
Temperature (K)	100	100
a, *b*, *c* (Å)	5.4534 (11), 17.203 (3), 20.060 (4)	23.840 (5), 9.7401 (19), 7.1403 (14)
V (Å^3)	1881.9 (6)	1658.0 (6)
Z	4	4
Radiation type	Synchrotron, λ = 0.96990 Å	Synchrotron, λ = 0.96990 Å
μ (mm^{-1})	0.43	0.52
Crystal size (mm)	0.20 × 0.15 × 0.10	0.20 × 0.05 × 0.03
Data collection		
Diffractometer	MAR CCD	MAR CCD
Absorption correction	Multi-scan (*SCALA*; Evans, 2006)	Multi-scan (*SCALA*; Evans, 2006)
T_{min}, T_{max}	0.910, 0.950	0.890, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13728, 3971, 3052	13537, 3464, 3127
R_{int}	0.095	0.073
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641	0.641
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.052, 0.123, 0.96	0.037, 0.090, 1.05
No. of reflections	3971	3464
No. of parameters	242	240
No. of restraints	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.39	0.25, −0.33
Absolute structure	Flack *x* determined using 997 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	Flack *x* determined using 1290 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.01 (4)	0.39 (2)

Computer programs: *Automar* (MarXperts, 2015), *iMosflm* (Battye *et al.*, 2011), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a MAR CCD detector. For each compound, a total of 360 images were collected using an oscillation range of 1.0° (φ scan mode) and corrected for absorption using the *SCALA* program (Evans, 2006). The data were indexed, integrated and scaled using the utility *i*MOSFLM in the program *CCP4* (Battye *et al.*, 2011).

The hydrogen atoms of the amino groups were localized in difference-Fourier maps and refined in isotropic approximation with the constraint $U_{iso}(H) = 1.2U_{eq}(N)$. The other hydrogen atoms were placed in calculated positions with C—H = 0.95–1.00 Å and refined using a riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl group and $1.2U_{eq}(C)$ for the other groups.

Acknowledgements

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supporting information

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Crystal structures of ethyl {2-[4-(4-isopropylphenyl)thiazol-2-yl]phenyl}-carbamate and ethyl {2-[4-(3-nitrophenyl)thiazol-2-yl]phenyl}carbamate

Elena V. Sukhonosova, Sergey A. Sokov, Gennady I. Ostapenko, Alexander S. Bunev, Pavel V. Dorovatovskii, Yan V. Zubavichus and Victor N. Khrustalev

Computing details

For both compounds, data collection: *Automar* (MarXperts, 2015); cell refinement: *iMosflm* (Battye *et al.*, 2011); data reduction: *iMosflm* (Battye *et al.*, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) Ethyl {2-[4-(4-isopropylphenyl)thiazol-2-yl]phenyl}carbamate

Crystal data

$C_{21}H_{22}N_2O_2S$
M_r = 366.47
Orthorhombic, $P2_12_12_1$
a = 5.4534 (11) Å
b = 17.203 (3) Å
c = 20.060 (4) Å
V = 1881.9 (6) Å^3
Z = 4
$F(000)$ = 776
D_x = 1.293 Mg m^{-3}
Synchrotron radiation, λ = 0.96990 Å
Cell parameters from 500 reflections
θ = 3.5–35.0°
μ = 0.43 mm^{-1}
T = 100 K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

MAR CCD diffractometer
phi scan
Absorption correction: multi-scan (SCALA; Evans, 2006)
T_{min} = 0.910, T_{max} = 0.950
13728 measured reflections
3971 independent reflections
3052 reflections with $I > 2\sigma(I)$
R_{int} = 0.095
θ_{max} = 38.5°, θ_{min} = 3.5°
h = −6→6
k = −20→21
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.123
S = 0.96
3971 reflections
242 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.004P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0210 (11)

Absolute structure: Flack *x* determined using 997 quotients $[(I^{+})-(I^{-})]/[(I^{+})+(I^{-})]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.01 (4)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.24911 (12)	0.47012 (3)	0.42460 (3)	0.03010 (16)
O1	1.2359 (3)	0.58830 (10)	0.61640 (9)	0.0352 (5)
O2	1.0633 (3)	0.47367 (9)	0.64975 (8)	0.0288 (4)
C2	0.4926 (5)	0.49392 (14)	0.47800 (12)	0.0259 (6)
N3	0.5248 (4)	0.44158 (11)	0.52534 (10)	0.0257 (5)
C4	0.3588 (4)	0.38088 (13)	0.52171 (12)	0.0239 (6)
C5	0.1972 (5)	0.38674 (14)	0.47016 (13)	0.0287 (7)
H5	0.0725	0.3498	0.4606	0.034*
C6	0.6380 (5)	0.56568 (14)	0.46990 (13)	0.0268 (6)
C7	0.8381 (5)	0.58484 (14)	0.51199 (12)	0.0257 (6)
N7	0.8934 (4)	0.53396 (11)	0.56480 (10)	0.0280 (5)
H7	0.787 (4)	0.4888 (14)	0.5664 (12)	0.034*
C8	0.9726 (5)	0.65255 (14)	0.50006 (13)	0.0319 (7)
H8	1.1061	0.6655	0.5284	0.038*
C9	0.9130 (5)	0.70106 (15)	0.44715 (13)	0.0350 (7)
H9	1.0076	0.7465	0.4392	0.042*
C10	0.7167 (5)	0.68374 (15)	0.40576 (14)	0.0367 (7)
H10	0.6744	0.7174	0.3700	0.044*
C11	0.5833 (5)	0.61661 (14)	0.41741 (13)	0.0329 (7)
H11	0.4498	0.6046	0.3888	0.039*
C12	1.0813 (5)	0.53798 (14)	0.61028 (12)	0.0261 (6)
C13	1.2512 (5)	0.46609 (14)	0.70045 (13)	0.0332 (7)
H13A	1.2590	0.5138	0.7280	0.040*
H13B	1.4134	0.4577	0.6795	0.040*
C14	1.1827 (5)	0.39723 (15)	0.74298 (13)	0.0364 (8)
H14A	1.1701	0.3508	0.7149	0.055*
H14B	1.0247	0.4071	0.7646	0.055*
H14C	1.3090	0.3891	0.7770	0.055*
C15	0.3725 (4)	0.31803 (13)	0.57234 (12)	0.0230 (6)
C16	0.5701 (5)	0.31297 (14)	0.61706 (12)	0.0262 (6)
H16	0.7017	0.3489	0.6138	0.031*
C17	0.5750 (5)	0.25610 (13)	0.66585 (13)	0.0265 (6)
H17	0.7105	0.2544	0.6956	0.032*
C18	0.3887 (5)	0.20128 (14)	0.67307 (12)	0.0257 (6)
C19	0.1953 (5)	0.20502 (14)	0.62699 (13)	0.0279 (7)

H19	0.0673	0.1676	0.6293	0.033*
C20	0.1868 (4)	0.26245 (13)	0.57785 (13)	0.0249 (6)
H20	0.0526	0.2638	0.5477	0.030*
C21	0.3936 (5)	0.14340 (14)	0.73046 (14)	0.0323 (7)
H21	0.5692	0.1301	0.7391	0.039*
C22	0.2582 (6)	0.06725 (13)	0.71601 (15)	0.0391 (7)
H22A	0.0830	0.0779	0.7101	0.059*
H22B	0.2810	0.0313	0.7534	0.059*
H22C	0.3241	0.0438	0.6752	0.059*
C23	0.2919 (6)	0.18119 (16)	0.79435 (14)	0.0446 (9)
H23A	0.3763	0.2306	0.8024	0.067*
H23B	0.3188	0.1463	0.8323	0.067*
H23C	0.1157	0.1907	0.7891	0.067*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0324 (3)	0.0306 (3)	0.0273 (3)	0.0019 (3)	−0.0031 (3)	−0.0005 (3)
O1	0.0338 (10)	0.0280 (8)	0.0438 (10)	−0.0087 (9)	−0.0062 (9)	0.0005 (8)
O2	0.0354 (10)	0.0240 (8)	0.0269 (9)	−0.0026 (8)	−0.0049 (8)	0.0034 (8)
C2	0.0264 (13)	0.0239 (12)	0.0275 (13)	0.0034 (12)	0.0057 (11)	−0.0012 (10)
N3	0.0304 (12)	0.0215 (9)	0.0252 (11)	−0.0013 (9)	0.0028 (9)	−0.0015 (8)
C4	0.0239 (13)	0.0204 (11)	0.0274 (13)	−0.0015 (11)	0.0020 (11)	−0.0061 (10)
C5	0.0271 (15)	0.0297 (12)	0.0293 (13)	0.0018 (12)	−0.0014 (11)	−0.0068 (11)
C6	0.0330 (15)	0.0250 (12)	0.0224 (13)	0.0036 (11)	0.0037 (11)	0.0001 (10)
C7	0.0312 (14)	0.0207 (11)	0.0253 (13)	0.0032 (11)	0.0040 (11)	0.0013 (10)
N7	0.0304 (12)	0.0245 (10)	0.0292 (11)	−0.0036 (10)	−0.0060 (10)	0.0024 (9)
C8	0.0353 (16)	0.0238 (12)	0.0367 (15)	−0.0024 (12)	0.0019 (13)	−0.0004 (11)
C9	0.0432 (16)	0.0241 (12)	0.0378 (15)	−0.0040 (13)	0.0107 (14)	0.0012 (12)
C10	0.0457 (17)	0.0308 (13)	0.0336 (14)	0.0004 (14)	0.0030 (14)	0.0080 (11)
C11	0.0376 (15)	0.0328 (13)	0.0282 (14)	0.0020 (13)	−0.0008 (13)	0.0019 (12)
C12	0.0275 (14)	0.0236 (12)	0.0274 (13)	0.0015 (12)	0.0010 (11)	−0.0013 (10)
C13	0.0336 (15)	0.0329 (13)	0.0330 (13)	0.0064 (15)	−0.0064 (13)	−0.0056 (11)
C14	0.0428 (18)	0.0380 (14)	0.0284 (14)	0.0119 (13)	−0.0025 (12)	−0.0002 (12)
C15	0.0221 (13)	0.0235 (11)	0.0234 (12)	0.0025 (10)	0.0014 (11)	−0.0056 (10)
C16	0.0252 (14)	0.0251 (12)	0.0283 (13)	−0.0009 (12)	0.0007 (11)	−0.0033 (10)
C17	0.0238 (13)	0.0261 (12)	0.0296 (13)	0.0017 (12)	0.0002 (12)	−0.0023 (11)
C18	0.0222 (13)	0.0224 (11)	0.0325 (14)	0.0026 (12)	0.0028 (12)	−0.0033 (11)
C19	0.0252 (15)	0.0227 (11)	0.0357 (14)	−0.0007 (12)	0.0013 (11)	−0.0035 (11)
C20	0.0233 (13)	0.0248 (11)	0.0267 (12)	0.0007 (10)	0.0006 (11)	−0.0056 (10)
C21	0.0278 (14)	0.0268 (12)	0.0424 (16)	−0.0013 (12)	−0.0010 (13)	0.0044 (12)
C22	0.0382 (16)	0.0303 (13)	0.0489 (16)	−0.0025 (14)	−0.0002 (16)	0.0083 (12)
C23	0.059 (2)	0.0388 (14)	0.0361 (16)	−0.0010 (16)	−0.0014 (15)	0.0080 (12)

Geometric parameters (Å, º)

S1—C5	1.724 (3)	C13—H13A	0.9900
S1—C2	1.755 (3)	C13—H13B	0.9900

O1—C12	1.215 (3)	C14—H14A	0.9800
O2—C12	1.364 (3)	C14—H14B	0.9800
O2—C13	1.449 (3)	C14—H14C	0.9800
C2—N3	1.320 (3)	C15—C20	1.397 (3)
C2—C6	1.476 (3)	C15—C16	1.405 (3)
N3—C4	1.384 (3)	C16—C17	1.384 (3)
C4—C5	1.362 (3)	C16—H16	0.9500
C4—C15	1.485 (3)	C17—C18	1.394 (3)
C5—H5	0.9500	C17—H17	0.9500
C6—C11	1.402 (3)	C18—C19	1.404 (4)
C6—C7	1.419 (4)	C18—C21	1.522 (4)
C7—C8	1.397 (3)	C19—C20	1.396 (3)
C7—N7	1.407 (3)	C19—H19	0.9500
N7—C12	1.374 (3)	C20—H20	0.9500
N7—H7	0.97 (2)	C21—C22	1.531 (4)
C8—C9	1.389 (4)	C21—C23	1.540 (4)
C8—H8	0.9500	C21—H21	1.0000
C9—C10	1.387 (4)	C22—H22A	0.9800
C9—H9	0.9500	C22—H22B	0.9800
C10—C11	1.385 (4)	C22—H22C	0.9800
C10—H10	0.9500	C23—H23A	0.9800
C11—H11	0.9500	C23—H23B	0.9800
C13—C14	1.507 (4)	C23—H23C	0.9800

C5—S1—C2	89.70 (12)	C13—C14—H14A	109.5
C12—O2—C13	115.43 (18)	C13—C14—H14B	109.5
N3—C2—C6	125.3 (2)	H14A—C14—H14B	109.5
N3—C2—S1	112.38 (18)	C13—C14—H14C	109.5
C6—C2—S1	122.31 (19)	H14A—C14—H14C	109.5
C2—N3—C4	112.9 (2)	H14B—C14—H14C	109.5
C5—C4—N3	114.0 (2)	C20—C15—C16	117.6 (2)
C5—C4—C15	127.3 (2)	C20—C15—C4	121.0 (2)
N3—C4—C15	118.7 (2)	C16—C15—C4	121.4 (2)
C4—C5—S1	110.96 (19)	C17—C16—C15	120.7 (2)
C4—C5—H5	124.5	C17—C16—H16	119.7
S1—C5—H5	124.5	C15—C16—H16	119.7
C11—C6—C7	117.7 (2)	C16—C17—C18	122.5 (2)
C11—C6—C2	119.4 (2)	C16—C17—H17	118.7
C7—C6—C2	122.8 (2)	C18—C17—H17	118.7
C8—C7—N7	122.4 (2)	C17—C18—C19	116.6 (2)
C8—C7—C6	119.7 (2)	C17—C18—C21	120.6 (2)
N7—C7—C6	117.9 (2)	C19—C18—C21	122.8 (2)
C12—N7—C7	128.9 (2)	C20—C19—C18	121.5 (2)
C12—N7—H7	117.8 (15)	C20—C19—H19	119.3
C7—N7—H7	113.2 (15)	C18—C19—H19	119.3
C9—C8—C7	120.6 (3)	C19—C20—C15	121.1 (2)
C9—C8—H8	119.7	C19—C20—H20	119.5
C7—C8—H8	119.7	C15—C20—H20	119.5

C10—C9—C8	120.6 (2)	C18—C21—C22	114.1 (2)
C10—C9—H9	119.7	C18—C21—C23	110.3 (2)
C8—C9—H9	119.7	C22—C21—C23	110.2 (2)
C11—C10—C9	118.9 (3)	C18—C21—H21	107.3
C11—C10—H10	120.5	C22—C21—H21	107.3
C9—C10—H10	120.5	C23—C21—H21	107.3
C10—C11—C6	122.4 (3)	C21—C22—H22A	109.5
C10—C11—H11	118.8	C21—C22—H22B	109.5
C6—C11—H11	118.8	H22A—C22—H22B	109.5
O1—C12—O2	124.7 (2)	C21—C22—H22C	109.5
O1—C12—N7	128.4 (2)	H22A—C22—H22C	109.5
O2—C12—N7	106.9 (2)	H22B—C22—H22C	109.5
O2—C13—C14	107.0 (2)	C21—C23—H23A	109.5
O2—C13—H13A	110.3	C21—C23—H23B	109.5
C14—C13—H13A	110.3	H23A—C23—H23B	109.5
O2—C13—H13B	110.3	C21—C23—H23C	109.5
C14—C13—H13B	110.3	H23A—C23—H23C	109.5
H13A—C13—H13B	108.6	H23B—C23—H23C	109.5

C5—S1—C2—N3	0.05 (19)	C2—C6—C11—C10	−178.1 (2)
C5—S1—C2—C6	−179.0 (2)	C13—O2—C12—O1	−2.2 (3)
C6—C2—N3—C4	178.7 (2)	C13—O2—C12—N7	178.51 (19)
S1—C2—N3—C4	−0.3 (3)	C7—N7—C12—O1	3.2 (4)
C2—N3—C4—C5	0.4 (3)	C7—N7—C12—O2	−177.5 (2)
C2—N3—C4—C15	−179.5 (2)	C12—O2—C13—C14	173.7 (2)
N3—C4—C5—S1	−0.4 (3)	C5—C4—C15—C20	−10.5 (4)
C15—C4—C5—S1	179.5 (2)	N3—C4—C15—C20	169.4 (2)
C2—S1—C5—C4	0.19 (19)	C5—C4—C15—C16	170.5 (2)
N3—C2—C6—C11	−179.7 (2)	N3—C4—C15—C16	−9.5 (3)
S1—C2—C6—C11	−0.8 (3)	C20—C15—C16—C17	−1.8 (3)
N3—C2—C6—C7	2.3 (4)	C4—C15—C16—C17	177.1 (2)
S1—C2—C6—C7	−178.8 (2)	C15—C16—C17—C18	0.4 (4)
C11—C6—C7—C8	−0.1 (4)	C16—C17—C18—C19	1.5 (4)
C2—C6—C7—C8	177.9 (2)	C16—C17—C18—C21	−175.7 (2)
C11—C6—C7—N7	179.9 (2)	C17—C18—C19—C20	−2.0 (4)
C2—C6—C7—N7	−2.1 (4)	C21—C18—C19—C20	175.1 (2)
C8—C7—N7—C12	−2.8 (4)	C18—C19—C20—C15	0.7 (4)
C6—C7—N7—C12	177.2 (2)	C16—C15—C20—C19	1.3 (3)
N7—C7—C8—C9	179.6 (2)	C4—C15—C20—C19	−177.7 (2)
C6—C7—C8—C9	−0.4 (4)	C17—C18—C21—C22	−153.4 (2)
C7—C8—C9—C10	0.9 (4)	C19—C18—C21—C22	29.5 (3)
C8—C9—C10—C11	−1.0 (4)	C17—C18—C21—C23	82.0 (3)
C9—C10—C11—C6	0.5 (4)	C19—C18—C21—C23	−95.1 (3)
C7—C6—C11—C10	0.0 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···N3	0.97 (2)	1.84 (2)	2.682 (3)	144 (2)
C8—H8···O1	0.95	2.32	2.954 (3)	124

(II) Ethyl {2-[4-(3-nitrophenyl)thiazol-2-yl]phenyl}carbamate

Crystal data

$C_{18}H_{15}N_3O_4S$
M_r = 369.39
Orthorhombic, $Pca2_1$
a = 23.840 (5) Å
b = 9.7401 (19) Å
c = 7.1403 (14) Å
V = 1658.0 (6) Å^3
Z = 4
$F(000)$ = 768
D_x = 1.480 Mg m^{-3}
Synchrotron radiation, λ = 0.96990 Å
Cell parameters from 600 reflections
θ = 3.7–37.0°
μ = 0.52 mm^{-1}
T = 100 K
Needle, colourless
0.20 × 0.05 × 0.03 mm

Data collection

MAR CCD diffractometer
phi scan
Absorption correction: multi-scan (SCALA; Evans, 2006)
T_{min} = 0.890, T_{max} = 0.980
13537 measured reflections
3464 independent reflections
3127 reflections with $I > 2\sigma(I)$
R_{int} = 0.073
θ_{max} = 38.5°, θ_{min} = 3.7°
h = −29→29
k = −12→12
l = −9→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.090
S = 1.05
3464 reflections
240 parameters
1 restraint
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.010 (2)
Absolute structure: Flack x determined using 1290 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.39 (2)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.82320 (2)	0.08743 (5)	0.40138 (11)	0.01687 (18)
O1	0.78056 (7)	0.74689 (17)	0.7251 (3)	0.0221 (5)
O2	0.69969 (7)	0.63003 (18)	0.6617 (3)	0.0183 (4)
O3	0.47989 (8)	−0.0296 (2)	0.3607 (4)	0.0367 (6)
O4	0.55366 (8)	−0.14517 (18)	0.2763 (3)	0.0279 (5)
C2	0.80673 (11)	0.2564 (2)	0.4636 (4)	0.0148 (5)
N3	0.75204 (10)	0.27926 (18)	0.4676 (3)	0.0155 (5)
C4	0.72122 (10)	0.1639 (2)	0.4202 (4)	0.0152 (5)
C5	0.75302 (11)	0.0509 (2)	0.3800 (4)	0.0172 (5)
H5	0.7383	−0.0360	0.3449	0.021*
C6	0.85019 (10)	0.3582 (2)	0.5131 (4)	0.0160 (5)
C7	0.83664 (11)	0.4896 (2)	0.5898 (4)	0.0148 (6)
N7	0.77977 (9)	0.5244 (2)	0.6077 (3)	0.0163 (5)
H7	0.7579 (13)	0.467 (3)	0.575 (5)	0.020*
C8	0.88015 (12)	0.5776 (2)	0.6456 (4)	0.0180 (6)
H8	0.8715	0.6643	0.6992	0.022*
C9	0.93587 (11)	0.5388 (3)	0.6230 (4)	0.0192 (6)
H9	0.9649	0.5992	0.6622	0.023*
C10	0.94981 (12)	0.4124 (2)	0.5438 (4)	0.0196 (6)
H10	0.9880	0.3873	0.5269	0.024*
C11	0.90696 (11)	0.3236 (2)	0.4899 (4)	0.0179 (6)
H11	0.9164	0.2375	0.4360	0.021*
C12	0.75647 (11)	0.6442 (2)	0.6700 (4)	0.0155 (5)
C13	0.66740 (11)	0.7511 (3)	0.7127 (4)	0.0202 (6)
H13A	0.6795	0.8311	0.6371	0.024*
H13B	0.6729	0.7731	0.8468	0.024*
C14	0.60652 (11)	0.7183 (3)	0.6745 (4)	0.0240 (6)
H14A	0.6015	0.6987	0.5409	0.036*
H14B	0.5832	0.7971	0.7096	0.036*
H14C	0.5953	0.6380	0.7482	0.036*
C15	0.65919 (10)	0.1740 (2)	0.4257 (4)	0.0157 (5)
C16	0.62493 (11)	0.0627 (2)	0.3740 (4)	0.0168 (6)
H16	0.6410	−0.0208	0.3311	0.020*
C17	0.56702 (10)	0.0777 (2)	0.3873 (4)	0.0173 (6)
N17	0.53118 (10)	−0.0404 (2)	0.3375 (4)	0.0216 (5)
C18	0.54099 (11)	0.1977 (3)	0.4468 (4)	0.0198 (6)
H18	0.5013	0.2042	0.4547	0.024*
C19	0.57550 (11)	0.3088 (2)	0.4949 (4)	0.0188 (6)
H19	0.5591	0.3927	0.5351	0.023*
C20	0.63338 (11)	0.2970 (2)	0.4843 (4)	0.0179 (6)
H20	0.6561	0.3734	0.5173	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0182 (3)	0.0103 (3)	0.0221 (4)	0.0010 (2)	−0.0001 (3)	−0.0034 (3)
O1	0.0226 (10)	0.0118 (9)	0.0320 (13)	−0.0024 (7)	−0.0008 (8)	−0.0069 (8)
O2	0.0139 (10)	0.0151 (9)	0.0260 (11)	0.0009 (7)	0.0029 (8)	−0.0035 (8)
O3	0.0206 (11)	0.0298 (11)	0.0596 (19)	−0.0090 (8)	0.0045 (11)	−0.0107 (11)
O4	0.0282 (11)	0.0123 (9)	0.0432 (14)	0.0024 (8)	−0.0086 (10)	−0.0063 (9)
C2	0.0186 (13)	0.0127 (11)	0.0131 (14)	0.0002 (10)	−0.0006 (9)	0.0000 (10)
N3	0.0187 (11)	0.0117 (9)	0.0160 (13)	−0.0007 (8)	0.0000 (9)	−0.0010 (8)
C4	0.0213 (12)	0.0104 (11)	0.0138 (14)	−0.0023 (9)	−0.0019 (11)	0.0003 (10)
C5	0.0206 (12)	0.0128 (10)	0.0181 (15)	−0.0025 (10)	−0.0009 (12)	−0.0018 (11)
C6	0.0199 (14)	0.0119 (12)	0.0161 (15)	0.0011 (10)	−0.0007 (11)	0.0014 (10)
C7	0.0152 (12)	0.0128 (12)	0.0165 (16)	0.0012 (9)	0.0014 (10)	0.0017 (10)
N7	0.0148 (11)	0.0094 (10)	0.0248 (14)	−0.0014 (8)	0.0019 (9)	−0.0050 (9)
C8	0.0219 (14)	0.0105 (12)	0.0215 (16)	−0.0008 (9)	−0.0019 (11)	−0.0002 (11)
C9	0.0185 (13)	0.0152 (12)	0.0240 (16)	−0.0027 (10)	−0.0013 (11)	0.0032 (11)
C10	0.0182 (14)	0.0176 (14)	0.0231 (16)	0.0003 (9)	0.0001 (11)	0.0009 (11)
C11	0.0210 (13)	0.0133 (12)	0.0194 (15)	0.0027 (9)	0.0010 (11)	−0.0001 (10)
C12	0.0184 (13)	0.0104 (11)	0.0177 (14)	0.0003 (10)	0.0004 (11)	0.0026 (10)
C13	0.0188 (13)	0.0136 (13)	0.0282 (17)	0.0063 (10)	0.0021 (12)	−0.0010 (12)
C14	0.0187 (13)	0.0273 (15)	0.0259 (18)	0.0029 (11)	0.0015 (11)	−0.0001 (12)
C15	0.0207 (13)	0.0110 (11)	0.0153 (14)	−0.0008 (9)	−0.0010 (11)	0.0029 (10)
C16	0.0212 (13)	0.0121 (11)	0.0170 (16)	0.0004 (9)	−0.0013 (11)	0.0008 (10)
C17	0.0200 (12)	0.0120 (11)	0.0200 (16)	−0.0050 (9)	−0.0009 (13)	0.0011 (11)
N17	0.0222 (12)	0.0145 (10)	0.0282 (15)	−0.0028 (9)	−0.0037 (10)	0.0005 (10)
C18	0.0199 (13)	0.0179 (13)	0.0215 (17)	−0.0013 (10)	−0.0011 (11)	0.0010 (11)
C19	0.0208 (13)	0.0115 (12)	0.0243 (15)	0.0006 (10)	0.0012 (11)	−0.0019 (11)
C20	0.0211 (13)	0.0133 (12)	0.0192 (14)	−0.0010 (10)	−0.0006 (11)	−0.0009 (10)

Geometric parameters (Å, º)

S1—C5	1.717 (3)	C9—H9	0.9500
S1—C2	1.750 (2)	C10—C11	1.393 (4)
O1—C12	1.218 (3)	C10—H10	0.9500
O2—C12	1.362 (3)	C11—H11	0.9500
O2—C13	1.455 (3)	C13—C14	1.511 (4)
O3—N17	1.239 (3)	C13—H13A	0.9900
O4—N17	1.233 (3)	C13—H13B	0.9900
C2—N3	1.323 (3)	C14—H14A	0.9800
C2—C6	1.477 (3)	C14—H14B	0.9800
N3—C4	1.385 (3)	C14—H14C	0.9800
C4—C5	1.367 (3)	C15—C16	1.406 (3)
C4—C15	1.482 (3)	C15—C20	1.411 (3)
C5—H5	0.9500	C16—C17	1.391 (3)
C6—C11	1.405 (3)	C16—H16	0.9500
C6—C7	1.429 (3)	C17—C18	1.390 (3)
C7—N7	1.404 (3)	C17—N17	1.477 (3)

C7—C8	1.403 (4)	C18—C19	1.402 (4)
N7—C12	1.367 (3)	C18—H18	0.9500
N7—H7	0.80 (3)	C19—C20	1.387 (4)
C8—C9	1.391 (4)	C19—H19	0.9500
C8—H8	0.9500	C20—H20	0.9500
C9—C10	1.395 (4)		

C5—S1—C2	89.94 (12)	O2—C12—N7	107.6 (2)
C12—O2—C13	115.65 (18)	O2—C13—C14	107.0 (2)
N3—C2—C6	125.0 (2)	O2—C13—H13A	110.3
N3—C2—S1	112.64 (17)	C14—C13—H13A	110.3
C6—C2—S1	122.34 (19)	O2—C13—H13B	110.3
C2—N3—C4	112.41 (19)	C14—C13—H13B	110.3
C5—C4—N3	114.2 (2)	H13A—C13—H13B	108.6
C5—C4—C15	127.8 (2)	C13—C14—H14A	109.5
N3—C4—C15	118.0 (2)	C13—C14—H14B	109.5
C4—C5—S1	110.78 (18)	H14A—C14—H14B	109.5
C4—C5—H5	124.6	C13—C14—H14C	109.5
S1—C5—H5	124.6	H14A—C14—H14C	109.5
C11—C6—C7	118.6 (2)	H14B—C14—H14C	109.5
C11—C6—C2	119.1 (2)	C16—C15—C20	118.6 (2)
C7—C6—C2	122.3 (2)	C16—C15—C4	121.4 (2)
N7—C7—C8	122.7 (2)	C20—C15—C4	120.0 (2)
N7—C7—C6	118.0 (2)	C17—C16—C15	118.5 (2)
C8—C7—C6	119.3 (2)	C17—C16—H16	120.7
C12—N7—C7	128.9 (2)	C15—C16—H16	120.7
C12—N7—H7	116 (2)	C18—C17—C16	123.5 (2)
C7—N7—H7	116 (2)	C18—C17—N17	118.1 (2)
C9—C8—C7	120.5 (2)	C16—C17—N17	118.4 (2)
C9—C8—H8	119.8	O4—N17—O3	123.2 (2)
C7—C8—H8	119.8	O4—N17—C17	118.6 (2)
C8—C9—C10	121.0 (2)	O3—N17—C17	118.2 (2)
C8—C9—H9	119.5	C17—C18—C19	117.5 (2)
C10—C9—H9	119.5	C17—C18—H18	121.3
C11—C10—C9	119.0 (2)	C19—C18—H18	121.3
C11—C10—H10	120.5	C20—C19—C18	120.5 (2)
C9—C10—H10	120.5	C20—C19—H19	119.8
C10—C11—C6	121.7 (2)	C18—C19—H19	119.8
C10—C11—H11	119.2	C19—C20—C15	121.4 (2)
C6—C11—H11	119.2	C19—C20—H20	119.3
O1—C12—O2	124.5 (2)	C15—C20—H20	119.3
O1—C12—N7	127.9 (2)		

C5—S1—C2—N3	0.4 (2)	C2—C6—C11—C10	−176.4 (3)
C5—S1—C2—C6	178.0 (2)	C13—O2—C12—O1	3.8 (4)
C6—C2—N3—C4	−178.0 (2)	C13—O2—C12—N7	−176.5 (2)
S1—C2—N3—C4	−0.4 (3)	C7—N7—C12—O1	−0.6 (5)
C2—N3—C4—C5	0.2 (3)	C7—N7—C12—O2	179.8 (2)

C2—N3—C4—C15	177.9 (2)	C12—O2—C13—C14	174.2 (2)
N3—C4—C5—S1	0.1 (3)	C5—C4—C15—C16	−4.7 (5)
C15—C4—C5—S1	−177.3 (2)	N3—C4—C15—C16	178.0 (3)
C2—S1—C5—C4	−0.3 (2)	C5—C4—C15—C20	175.1 (3)
N3—C2—C6—C11	−175.5 (2)	N3—C4—C15—C20	−2.2 (4)
S1—C2—C6—C11	7.2 (4)	C20—C15—C16—C17	−1.5 (4)
N3—C2—C6—C7	6.7 (4)	C4—C15—C16—C17	178.3 (3)
S1—C2—C6—C7	−170.7 (2)	C15—C16—C17—C18	0.8 (4)
C11—C6—C7—N7	178.4 (2)	C15—C16—C17—N17	−178.5 (3)
C2—C6—C7—N7	−3.7 (4)	C18—C17—N17—O4	176.7 (3)
C11—C6—C7—C8	−2.3 (4)	C16—C17—N17—O4	−3.9 (4)
C2—C6—C7—C8	175.6 (2)	C18—C17—N17—O3	−3.9 (4)
C8—C7—N7—C12	3.2 (5)	C16—C17—N17—O3	175.5 (3)
C6—C7—N7—C12	−177.5 (3)	C16—C17—C18—C19	0.3 (4)
N7—C7—C8—C9	−179.3 (3)	N17—C17—C18—C19	179.6 (2)
C6—C7—C8—C9	1.3 (4)	C17—C18—C19—C20	−0.6 (4)
C7—C8—C9—C10	0.4 (4)	C18—C19—C20—C15	−0.1 (4)
C8—C9—C10—C11	−1.1 (4)	C16—C15—C20—C19	1.2 (4)
C9—C10—C11—C6	0.1 (4)	C4—C15—C20—C19	−178.6 (2)
C7—C6—C11—C10	1.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{i}	0.95	2.32	3.260 (3)	168
N7—H7···N3	0.80 (3)	1.98 (3)	2.672 (3)	144 (3)
C8—H8···O1	0.95	2.32	2.946 (3)	123

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