Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-(2-Nitrophenyl)thiophene-2-carboxamide

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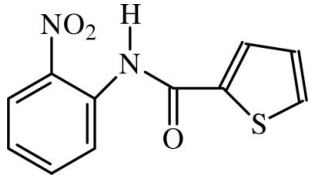
Received 22 April 2014; accepted 22 April 2014

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.004 Å; R factor = 0.047; wR factor = 0.116; data-to-parameter ratio = 16.2.

The title compound, $C_{11}H_8N_2O_3S$, shows two molecules per asymmetric unit, with the dihedral angles between the benzene and thiophene rings of 13.53 (6) and 8.50 (5)° being a notable difference between them. An intramolecular N—H···O hydrogen-bond in each molecule generates an S(6) ring motif. The crystal packing shows no classical hydrogen bonds with the molecules being packed to form weak C—H···O and C—H···S interactions leading to $R_2^2(9)$ and $R_4^4(25)$ rings which are edge-shared, giving layers parallel to (010).

Related literature

For the antibacterial and antifungal activity of amide compounds, see: Aytemir *et al.* (2003); Hrelia *et al.* (1995). For a similar compound, see: Moreno-Fuquen *et al.* (2013). For hydrogen-bonding information, see: Nardelli (1995). For hydrogen-bond motifs, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_{11}H_8N_2O_3S$
M_r = 248.25
Monoclinic, $P2_1/c$
a = 11.6359 (3) Å
b = 13.2501 (3) Å
c = 17.7412 (4) Å
β = 129.898 (1)°
V = 2098.47 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 123 K
0.28 × 0.15 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur E diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
T_{min} = 0.953, T_{max} = 1.000
10418 measured reflections
5093 independent reflections
4012 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.116
S = 1.04
5093 reflections
315 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O2	0.81 (3)	1.96 (3)	2.634 (2)	140 (3)
N3—H3*N*···O5	0.84 (2)	1.93 (2)	2.616 (2)	138 (2)
C1—H1···O4^{i}	0.95	2.50	3.209 (3)	131
C8—H8···O5^{ii}	0.95	2.52	3.248 (3)	133
C19—H19···O2^{iii}	0.95	2.63	3.377 (3)	136
C11—H11···S2^{iii}	0.95	2.92	3.732 (2)	144
C22—H22···S1^{ii}	0.95	2.84	3.689 (2)	149
C12—H12···O1^{iv}	0.95	2.47	3.198 (3)	133

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

RMF thanks the Universidad del Valle, Colombia, for partial financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5309).

References

Aytemir, M. D., Hider, R. C., Erol, D. D., Ozalp, M. & Ekizoglu, M. (2003). *Turk. J. Chem.* **27**, 445–452.
Etter, M. (1990). *Acc. Chem. Res.* **23**, 120–126.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Hrelia, P., Vigagni, F., Maffei, F., Fimognari, C., Lamartina, L., Spinelli, D., Juric, P., Guerra, M. C. & Cantelli-Forti, G. (1995). *Mutagenesis*, **10**, 171–177.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Moreno-Fuquen, R., Azcárate, A., Kennedy, A. R., Gilmour, D. & De Almeida Santos, R. H. (2013). *Acta Cryst.* E**69**, o1592.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2014). E**70**, o613 [doi:10.1107/S160053681400912X]

N-(2-Nitrophenyl)thiophene-2-carboxamide

Rodolfo Moreno-Fuquen, Alexis Azcárate and Alan R. Kennedy

S1. Experimental

S1.1. Synthesis and crystallization

The reagents and solvents for the synthesis were obtained from the Aldrich Chemical Co., and were used without additional purification. The title molecule was synthesized using equimolar quantities of 2-thiophenecarbonyl chloride (0.376 g., 2.565 mmol) and 2-nitroaniline (0.354 g). The reagents were dissolved in 10 mL of acetonitrile and the solution was taken to reflux in constant stirring for 1 hour. Yellow crystals of good quality were obtained after leaving the solvent to evaporate. M.pt: 397 (1) K.

S1.2. Refinement

All H-atoms were positioned at geometrically idealized positions with a C—H distance of 0.95 Å and U_{iso}(H) = 1.2U_{eq} of the atoms to which they were bonded. The H1N and H3N atoms were found from Fourier maps and were refined freely.

S2. Results and discussion

The present compound forms part of a systematic work on N-aromatic amides in our research group. Antibacterial and antifungal activities of different carboxyamide derivatives have been reported (Aytemir *et al.*, 2003). Derivatives of thiophene carboxanilide compounds present genotoxicity in bacterial mammalian and human cells (Hrelia *et al.*, 1995). In the synthesis of the amides, the 2-nitroaniline is taken as a template, in order to study the structural changes and the supramolecular behavior by the reaction of different ligands with this precursor (Moreno-Fuquen *et al.*, 2013). With this aim, the synthesis of N-(2-nitrophenyl)thiophene-2-carboxamide (I) was undertaken. The structure of N-(2-nitrophenyl)-furan-2-carboxamide (2NPFC), (Moreno-Fuquen *et al.*, 2013), a similar compound, was taken to compare with the structural parameters of (I).

The title compound shows two molecules (A and B) per asymmetric unit (see Fig. 1). Compound (I) exhibits dihedral angles between the benzene and thiophene rings of 13.53 (6)° and 8.50 (5)° for A and B, respectively. These dihedral angles are very similar to the value presented in the (2NPFC) system [9.71 (5)°]. The other bond lengths and bond angles agree closely with those values presented in its homologous amide (2NPFC), except for the C—S distances, which for obvious reasons are different on the furan rings. The nitro groups form dihedral angles with the adjacent benzene ring of 15.44 (4) and 16.07 (6)° for O2—N2—O3 and O5—N4—O6, respectively.

The crystal packing shows no classical hydrogen bonds and the molecules are packed forming weak C—H···O and C—H···S interactions and they are propagated parallel to (010) (see Fig. 2). According to the graph-set assignment, the intramolecular hydrogen-bond pattern generates a S(6) ring motif (Etter, 1990) (see Table 1). The C8 and C11 atoms of the phenyl ring and C1 atom of the thiophene ring at (*x*, *y*, *z*), act as hydrogen-bond donors to the nitro O5 atom at (*x*, -*y*+3/2, +*z*+1/2), to the S2 atom at (*x*-1, -*y*+3/2, +*z*-1/2) and to the carbonyl atom O4 at (*x*, -*y*+3/2, +*z*-1/2), respectively. Additionally, the C19 and C22 atoms of the benzene ring and C12 atom of the thiophene ring at (*x*, *y*, *z*) act as hydrogen-

bond donors to the nitro O2 atom at (*x*-1, -*y*+3/2, +*z*-1/2), to the S1 atom at (*x*, -*y*+3/2, +*z*+1/2) and to the carbonyl O1 atom at (*x*+1, -*y*+3/2, +*z*+1/2), respectively, (see Table 1; Nardelli, 1995). All these interactions form an $R^2_2(9)$ and $R^4_4(25)$ edge-fused ring which are running parallel to (010) (see Fig. 2).

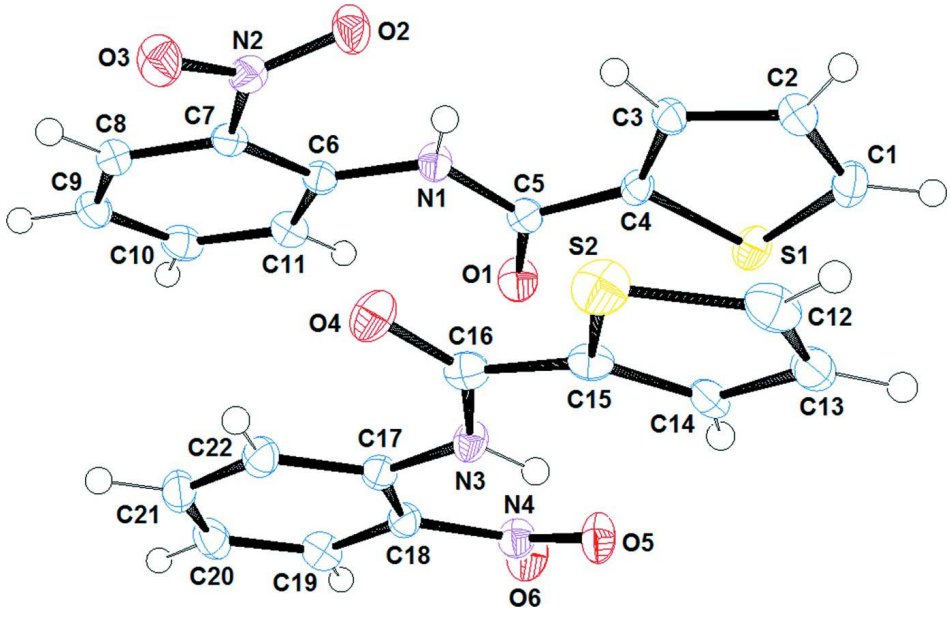


Figure 1

Molecular conformation and atom numbering scheme for the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

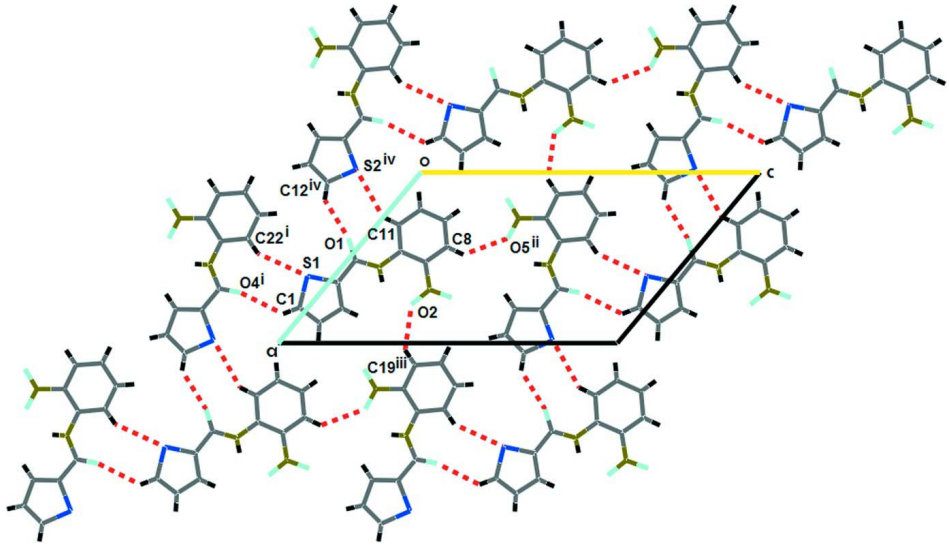


Figure 2

Part of the crystal structure of (I), showing the formation of edge-fused $R^2_2(9)$ and $R^4_4(25)$ rings running parallel to (010).

N-(2-Nitrophenyl)thiophene-2-carboxamide

Crystal data

$C_{11}H_8N_2O_3S$
$M_r = 248.25$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.6359$ (3) Å
$b = 13.2501$ (3) Å
$c = 17.7412$ (4) Å
$\beta = 129.898$ (1)°
$V = 2098.47$ (9) Å^3
$Z = 8$
$F(000) = 1024$
$D_x = 1.572$ Mg m^{-3}
Melting point: 397(1) K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4181 reflections
$\theta = 3.4$–29.4°
$\mu = 0.31$ mm^{-1}
$T = 123$ K
Tablet, yellow
0.28 × 0.15 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur E diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{min} = 0.953$, $T_{max} = 1.000$
10418 measured reflections
5093 independent reflections
4012 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 29.4°$, $\theta_{min} = 3.4°$
$h = -15\rightarrow14$
$k = -15\rightarrow17$
$l = -22\rightarrow24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.116$
$S = 1.04$
5093 reflections
315 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.7613P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ 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 $F^2 > \sigma(F^2)$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.60696 (6)	0.81889 (4)	−0.07981 (4)	0.02441 (14)
S2	0.98321 (6)	0.64159 (5)	0.30229 (4)	0.03015 (16)
O1	0.38729 (16)	0.85064 (13)	−0.05031 (11)	0.0255 (4)

O2	0.77371 (16)	0.93931 (13)	0.29784 (11)	0.0262 (4)
O3	0.73314 (17)	0.91094 (13)	0.39862 (11)	0.0274 (4)
O4	0.70355 (17)	0.70186 (12)	0.26329 (11)	0.0269 (4)
O5	0.38579 (16)	0.59679 (13)	−0.08094 (11)	0.0268 (4)
O6	0.15254 (17)	0.63885 (14)	−0.18258 (11)	0.0303 (4)
N1	0.5542 (2)	0.90436 (14)	0.10981 (13)	0.0184 (4)
N2	0.68724 (19)	0.92377 (13)	0.31503 (12)	0.0193 (4)
N3	0.54164 (19)	0.64179 (14)	0.10488 (13)	0.0189 (4)
N4	0.26905 (19)	0.62585 (14)	−0.09860 (13)	0.0217 (4)
C1	0.7915 (3)	0.82021 (17)	−0.02508 (16)	0.0247 (5)
H1	0.8288	0.8029	−0.0578	0.030*
C2	0.8804 (2)	0.84884 (17)	0.07096 (16)	0.0220 (4)
H2	0.9864	0.8533	0.1126	0.026*
C3	0.7965 (2)	0.87137 (16)	0.10222 (15)	0.0182 (4)
H3	0.8395	0.8922	0.1667	0.022*
C4	0.6440 (2)	0.85876 (15)	0.02591 (14)	0.0171 (4)
C5	0.5153 (2)	0.87066 (16)	0.02341 (14)	0.0180 (4)
C6	0.4632 (2)	0.91537 (15)	0.13495 (14)	0.0171 (4)
C7	0.5258 (2)	0.92336 (15)	0.23390 (15)	0.0173 (4)
C8	0.4367 (2)	0.93183 (16)	0.26042 (16)	0.0218 (4)
H8	0.4816	0.9355	0.3278	0.026*
C9	0.2828 (2)	0.93496 (17)	0.18862 (17)	0.0240 (5)
H9	0.2211	0.9416	0.2060	0.029*
C10	0.2195 (2)	0.92823 (17)	0.09095 (16)	0.0230 (5)
H10	0.1136	0.9307	0.0414	0.028*
C11	0.3066 (2)	0.91801 (16)	0.06396 (15)	0.0200 (4)
H11	0.2599	0.9127	−0.0036	0.024*
C12	1.0568 (2)	0.60694 (18)	0.24879 (17)	0.0268 (5)
H12	1.1610	0.5988	0.2838	0.032*
C13	0.9500 (2)	0.59212 (17)	0.15022 (16)	0.0230 (5)
H13	0.9720	0.5724	0.1092	0.028*
C14	0.8015 (2)	0.60940 (16)	0.11495 (15)	0.0185 (4)
H14	0.7132	0.6030	0.0483	0.022*
C15	0.8039 (2)	0.63702 (16)	0.19220 (14)	0.0188 (4)
C16	0.6807 (2)	0.66372 (16)	0.19215 (15)	0.0194 (4)
C17	0.4018 (2)	0.65097 (15)	0.08063 (14)	0.0172 (4)
C18	0.2688 (2)	0.64194 (16)	−0.01743 (15)	0.0182 (4)
C19	0.1290 (2)	0.64708 (17)	−0.04208 (16)	0.0232 (5)
H19	0.0408	0.6408	−0.1088	0.028*
C20	0.1180 (3)	0.66121 (17)	0.03006 (18)	0.0256 (5)
H20	0.0227	0.6636	0.0137	0.031*
C21	0.2479 (3)	0.67189 (17)	0.12687 (17)	0.0240 (5)
H21	0.2409	0.6827	0.1767	0.029*
C22	0.3873 (2)	0.66709 (16)	0.15197 (16)	0.0212 (4)
H22	0.4747	0.6749	0.2187	0.025*
H3N	0.536 (3)	0.6175 (18)	0.0592 (18)	0.020 (6)*
H1N	0.642 (3)	0.914 (2)	0.156 (2)	0.033 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0264 (3)	0.0289 (3)	0.0169 (2)	0.0012 (2)	0.0134 (2)	−0.0021 (2)
S2	0.0209 (3)	0.0372 (4)	0.0198 (3)	−0.0010 (2)	0.0073 (2)	−0.0030 (2)
O1	0.0176 (7)	0.0359 (9)	0.0171 (7)	−0.0009 (7)	0.0085 (6)	−0.0018 (6)
O2	0.0178 (7)	0.0417 (10)	0.0203 (7)	−0.0054 (7)	0.0129 (6)	−0.0059 (7)
O3	0.0270 (8)	0.0359 (9)	0.0166 (7)	−0.0021 (7)	0.0128 (7)	0.0020 (7)
O4	0.0264 (8)	0.0321 (9)	0.0173 (7)	0.0015 (7)	0.0118 (6)	−0.0039 (7)
O5	0.0185 (7)	0.0425 (10)	0.0209 (7)	−0.0019 (7)	0.0134 (6)	−0.0061 (7)
O6	0.0232 (8)	0.0442 (10)	0.0150 (7)	0.0044 (7)	0.0084 (6)	0.0006 (7)
N1	0.0128 (8)	0.0254 (10)	0.0147 (8)	−0.0009 (7)	0.0077 (7)	−0.0020 (7)
N2	0.0199 (8)	0.0193 (9)	0.0179 (8)	−0.0012 (7)	0.0117 (7)	−0.0020 (7)
N3	0.0182 (8)	0.0236 (9)	0.0138 (8)	−0.0002 (7)	0.0098 (7)	−0.0025 (7)
N4	0.0191 (9)	0.0257 (10)	0.0179 (8)	−0.0016 (8)	0.0109 (7)	−0.0025 (7)
C1	0.0308 (12)	0.0253 (11)	0.0261 (11)	0.0032 (10)	0.0220 (10)	0.0014 (9)
C2	0.0204 (10)	0.0241 (11)	0.0230 (10)	−0.0010 (9)	0.0147 (9)	0.0006 (9)
C3	0.0210 (10)	0.0174 (10)	0.0203 (10)	−0.0003 (8)	0.0150 (9)	0.0010 (8)
C4	0.0213 (10)	0.0165 (10)	0.0148 (9)	0.0010 (8)	0.0122 (8)	0.0008 (7)
C5	0.0205 (10)	0.0170 (10)	0.0159 (9)	0.0011 (8)	0.0114 (8)	0.0024 (8)
C6	0.0191 (10)	0.0150 (10)	0.0183 (9)	0.0004 (8)	0.0125 (8)	0.0012 (8)
C7	0.0166 (9)	0.0154 (10)	0.0191 (9)	−0.0010 (8)	0.0112 (8)	−0.0005 (8)
C8	0.0268 (11)	0.0205 (11)	0.0243 (10)	−0.0044 (9)	0.0191 (9)	−0.0035 (8)
C9	0.0243 (11)	0.0228 (11)	0.0336 (12)	−0.0039 (9)	0.0225 (10)	−0.0041 (9)
C10	0.0167 (10)	0.0220 (11)	0.0268 (11)	−0.0008 (9)	0.0124 (9)	0.0003 (9)
C11	0.0178 (10)	0.0200 (10)	0.0192 (10)	0.0012 (8)	0.0106 (8)	0.0026 (8)
C12	0.0165 (10)	0.0279 (12)	0.0274 (11)	−0.0012 (9)	0.0102 (9)	0.0028 (9)
C13	0.0225 (10)	0.0215 (11)	0.0275 (11)	−0.0006 (9)	0.0172 (9)	0.0016 (9)
C14	0.0160 (9)	0.0175 (10)	0.0232 (10)	0.0005 (8)	0.0131 (8)	0.0041 (8)
C15	0.0168 (9)	0.0171 (10)	0.0157 (9)	−0.0015 (8)	0.0073 (8)	0.0006 (8)
C16	0.0213 (10)	0.0162 (10)	0.0156 (9)	0.0012 (8)	0.0095 (8)	0.0033 (8)
C17	0.0186 (10)	0.0158 (10)	0.0174 (9)	0.0009 (8)	0.0117 (8)	0.0015 (8)
C18	0.0214 (10)	0.0172 (10)	0.0175 (9)	0.0006 (8)	0.0132 (8)	0.0008 (8)
C19	0.0203 (10)	0.0234 (11)	0.0233 (10)	0.0007 (9)	0.0128 (9)	0.0026 (9)
C20	0.0254 (11)	0.0236 (11)	0.0375 (13)	0.0031 (9)	0.0246 (10)	0.0047 (10)
C21	0.0334 (12)	0.0210 (11)	0.0293 (11)	0.0036 (9)	0.0255 (10)	0.0033 (9)
C22	0.0265 (11)	0.0202 (11)	0.0193 (10)	0.0021 (9)	0.0158 (9)	0.0022 (8)

Geometric parameters (Å, º)

S1—C1	1.697 (2)	C6—C11	1.401 (3)
S1—C4	1.716 (2)	C6—C7	1.408 (3)
S2—C12	1.699 (3)	C7—C8	1.391 (3)
S2—C15	1.716 (2)	C8—C9	1.380 (3)
O1—C5	1.225 (2)	C8—H8	0.9500
O2—N2	1.242 (2)	C9—C10	1.384 (3)
O3—N2	1.224 (2)	C9—H9	0.9500
O4—C16	1.220 (3)	C10—C11	1.376 (3)

O5—N4	1.243 (2)	C10—H10	0.9500
O6—N4	1.223 (2)	C11—H11	0.9500
N1—C5	1.366 (3)	C12—C13	1.361 (3)
N1—C6	1.395 (3)	C12—H12	0.9500
N1—H1N	0.81 (3)	C13—C14	1.430 (3)
N2—O2	1.242 (2)	C13—H13	0.9500
N2—C7	1.460 (3)	C14—C15	1.401 (3)
N3—C16	1.373 (3)	C14—H14	0.9500
N3—C17	1.396 (3)	C15—C16	1.476 (3)
N3—H3N	0.84 (2)	C17—C22	1.396 (3)
N4—O5	1.243 (2)	C17—C18	1.408 (3)
N4—C18	1.457 (3)	C18—C19	1.390 (3)
C1—C2	1.362 (3)	C19—C20	1.378 (3)
C1—H1	0.9500	C19—H19	0.9500
C2—C3	1.429 (3)	C20—C21	1.387 (3)
C2—H2	0.9500	C20—H20	0.9500
C3—C4	1.388 (3)	C21—C22	1.381 (3)
C3—H3	0.9500	C21—H21	0.9500
C4—C5	1.478 (3)	C22—H22	0.9500

C1—S1—C4	91.88 (10)	C8—C9—C10	119.2 (2)
C12—S2—C15	92.00 (11)	C8—C9—H9	120.4
C5—N1—C6	128.35 (18)	C10—C9—H9	120.4
C5—N1—H1N	118.8 (19)	C11—C10—C9	121.5 (2)
C6—N1—H1N	112.4 (19)	C11—C10—H10	119.3
O3—N2—O2	121.89 (17)	C9—C10—H10	119.3
O3—N2—O2	121.89 (17)	C10—C11—C6	120.8 (2)
O3—N2—C7	118.65 (17)	C10—C11—H11	119.6
O2—N2—C7	119.44 (17)	C6—C11—H11	119.6
O2—N2—C7	119.44 (17)	C13—C12—S2	112.66 (17)
C16—N3—C17	128.81 (18)	C13—C12—H12	123.7
C16—N3—H3N	118.3 (16)	S2—C12—H12	123.7
C17—N3—H3N	112.9 (16)	C12—C13—C14	112.9 (2)
O6—N4—O5	121.92 (18)	C12—C13—H13	123.5
O6—N4—O5	121.92 (18)	C14—C13—H13	123.5
O6—N4—C18	118.68 (18)	C15—C14—C13	110.71 (18)
O5—N4—C18	119.36 (17)	C15—C14—H14	124.6
O5—N4—C18	119.36 (17)	C13—C14—H14	124.6
C2—C1—S1	112.67 (17)	C14—C15—C16	130.68 (18)
C2—C1—H1	123.7	C14—C15—S2	111.69 (16)
S1—C1—H1	123.7	C16—C15—S2	117.62 (15)
C1—C2—C3	112.57 (19)	O4—C16—N3	124.8 (2)
C1—C2—H2	123.7	O4—C16—C15	122.12 (19)
C3—C2—H2	123.7	N3—C16—C15	113.07 (18)
C4—C3—C2	111.11 (18)	C22—C17—N3	121.89 (18)
C4—C3—H3	124.4	C22—C17—C18	117.21 (19)
C2—C3—H3	124.4	N3—C17—C18	120.89 (18)
C3—C4—C5	130.78 (18)	C19—C18—C17	121.45 (19)

C3—C4—S1	111.76 (15)	C19—C18—N4	116.11 (18)
C5—C4—S1	117.42 (15)	C17—C18—N4	122.44 (18)
O1—C5—N1	124.7 (2)	C20—C19—C18	120.1 (2)
O1—C5—C4	121.59 (19)	C20—C19—H19	119.9
N1—C5—C4	113.69 (17)	C18—C19—H19	119.9
N1—C6—C11	122.09 (18)	C19—C20—C21	119.1 (2)
N1—C6—C7	120.96 (18)	C19—C20—H20	120.4
C11—C6—C7	116.95 (18)	C21—C20—H20	120.4
C8—C7—C6	121.73 (19)	C22—C21—C20	121.1 (2)
C8—C7—N2	115.67 (18)	C22—C21—H21	119.4
C6—C7—N2	122.60 (18)	C20—C21—H21	119.4
C9—C8—C7	119.8 (2)	C21—C22—C17	121.0 (2)
C9—C8—H8	120.1	C21—C22—H22	119.5
C7—C8—H8	120.1	C17—C22—H22	119.5

O2—O2—N2—O3	0.0 (5)	N1—C6—C11—C10	179.5 (2)
O2—O2—N2—C7	0.0 (5)	C7—C6—C11—C10	0.1 (3)
O5—O5—N4—O6	0.00 (11)	C15—S2—C12—C13	0.07 (19)
O5—O5—N4—C18	0.00 (6)	S2—C12—C13—C14	0.1 (3)
C4—S1—C1—C2	0.65 (18)	C12—C13—C14—C15	−0.4 (3)
S1—C1—C2—C3	−0.3 (3)	C13—C14—C15—C16	178.9 (2)
C1—C2—C3—C4	−0.3 (3)	C13—C14—C15—S2	0.4 (2)
C2—C3—C4—C5	178.5 (2)	C12—S2—C15—C14	−0.27 (17)
C2—C3—C4—S1	0.8 (2)	C12—S2—C15—C16	−178.96 (17)
C1—S1—C4—C3	−0.82 (17)	C17—N3—C16—O4	−4.7 (4)
C1—S1—C4—C5	−178.85 (17)	C17—N3—C16—C15	175.74 (19)
C6—N1—C5—O1	5.4 (4)	C14—C15—C16—O4	−167.8 (2)
C6—N1—C5—C4	−174.01 (19)	S2—C15—C16—O4	10.6 (3)
C3—C4—C5—O1	−175.9 (2)	C14—C15—C16—N3	11.8 (3)
S1—C4—C5—O1	1.7 (3)	S2—C15—C16—N3	−169.80 (15)
C3—C4—C5—N1	3.6 (3)	C16—N3—C17—C22	−12.8 (3)
S1—C4—C5—N1	−178.86 (15)	C16—N3—C17—C18	168.7 (2)
C5—N1—C6—C11	−17.6 (3)	C22—C17—C18—C19	−1.1 (3)
C5—N1—C6—C7	161.8 (2)	N3—C17—C18—C19	177.51 (19)
N1—C6—C7—C8	−178.37 (19)	C22—C17—C18—N4	179.48 (19)
C11—C6—C7—C8	1.0 (3)	N3—C17—C18—N4	−1.9 (3)
N1—C6—C7—N2	1.9 (3)	O6—N4—C18—C19	15.1 (3)
C11—C6—C7—N2	−178.70 (19)	O5—N4—C18—C19	−162.99 (19)
O3—N2—C7—C8	14.5 (3)	O5—N4—C18—C19	−162.99 (19)
O2—N2—C7—C8	−163.90 (19)	O6—N4—C18—C17	−165.5 (2)
O2—N2—C7—C8	−163.90 (19)	O5—N4—C18—C17	16.5 (3)
O3—N2—C7—C6	−165.80 (19)	O5—N4—C18—C17	16.5 (3)
O2—N2—C7—C6	15.8 (3)	C17—C18—C19—C20	−0.1 (3)
O2—N2—C7—C6	15.8 (3)	N4—C18—C19—C20	179.4 (2)
C6—C7—C8—C9	−1.5 (3)	C18—C19—C20—C21	1.1 (3)
N2—C7—C8—C9	178.20 (19)	C19—C20—C21—C22	−1.0 (3)
C7—C8—C9—C10	0.8 (3)	C20—C21—C22—C17	−0.2 (3)
C8—C9—C10—C11	0.3 (3)	N3—C17—C22—C21	−177.4 (2)

C9—C10—C11—C6	−0.8 (3)	C18—C17—C22—C21	1.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O2	0.81 (3)	1.96 (3)	2.634 (2)	140 (3)
N3—H3*N*···O5	0.84 (2)	1.93 (2)	2.616 (2)	138 (2)
C1—H1···O4^{i}	0.95	2.50	3.209 (3)	131
C8—H8···O5^{ii}	0.95	2.52	3.248 (3)	133
C19—H19···O2^{iii}	0.95	2.63	3.377 (3)	136
C11—H11···S2^{iii}	0.95	2.92	3.732 (2)	144
C22—H22···S1^{ii}	0.95	2.84	3.689 (2)	149
C12—H12···O1^{iv}	0.95	2.47	3.198 (3)	133

Symmetry codes: (i) x, $-y+3/2$, $z-1/2$; (ii) x, $-y+3/2$, $z+1/2$; (iii) $x-1$, $-y+3/2$, $z-1/2$; (iv) $x+1$, $-y+3/2$, $z+1/2$.