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(2*Z*)-2-Benzylidene-4-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-3,4-dihydro-2*H*-1,4-benzothiazin-3-one

Nada Kheira Sebbar,[a] Mohamed Ellouz,[a]* Mohammed Boulhaoua,[a] Younes Ouzidan,[b] El Mokhtar Essassi[a] and Joel T. Mague[c]

[a]Laboratoire de Chimie Organique Hétérocyclique URAC 21, Pôle de Compétence Pharmacochimie, Av. Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, [b]Laboratoire de Chimie Organique Appliquée, Université Sidi Mohamed Ben Abdallah, Faculté des Sciences et Techniques, Route d'Imouzzer, BP 2202, Fez, Morocco, and [c]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: ellouz.chimie@gmail.com

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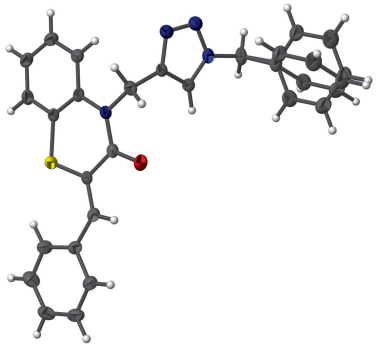
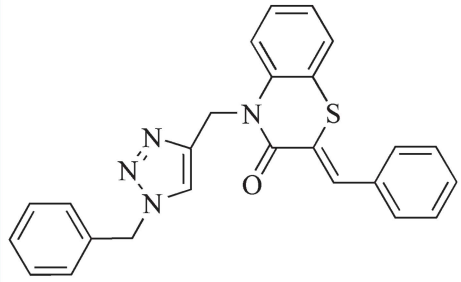
In the title molecule, $C_{25}H_{20}N_4OS$, the dihedral angle between the plane of the dihydrothiazine ring and that of the fused C_6 ring is 1.0 (2)°, indicating a slight twist in the dihydrobenzothiophene unit; there is a roughly perpendicular relationship between the fused C_6 ring and the triazole ring [dihedral angle = 73.2 (1)°]. The packing comprises chains running parallel to the *c* axis formed by weak C—H···O hydrogen bonds, with the benzyl rings intercalated between adjacent chains. The benzyl ring is statistically disordered. The sample was refined as a twin.

3D view



Chemical scheme



Structure description

1,4-Benzothiazine derivatives possess a wide spectrum of biological and pharmacological activities due to the presence of a fold along the nitrogen···sulfur axis, considered to be one of the structural features responsible for their activities (Gupta & Gupta, 2011). A variety of methods have been used to synthesize 1,4-benzothiazine derivatives (Parai & Panda, 2009; Saadouni *et al.*, 2014). Some of the diverse biological activities exhibited by 1,4-benzothiazines (Fringuelli *et al.*, 2005) are as antimicrobial (Gautam *et al.*, 2013), antifungal (Aloui *et al.*, 2009) and anti-oxidant agents (Kumar *et al.*, 2010) as well as acting as inhibitors of betaribosidases (Gao & Hollingsworth, 2005), as potential vaso-dilators (Deshmukh & Mulik, 2004) and as potent lipoxygenase inhibitors (Bakavoli *et al.*, 2007). In addition, 1,4-benzothiazines are the basis for novel dyes (Podsiadły, 2009).

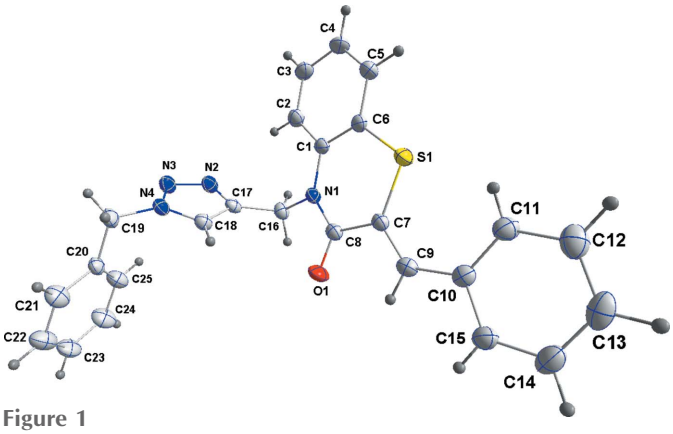


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids.

Some relevant structures of 1,4-benzothiazine derivatives have been published (Ellouz, *et al.*, 2015; Sebbar *et al.*, 2014; Zerzouf *et al.*, 2001).

As a continuation of our studies of substituted 1,4-benzothiazine derivatives (Ellouz *et al.*, 2015; Sebbar *et al.*, 2015), we report the synthesis of a new 1,4-benzothiazine derivative which is built from two fused six-membered rings linked to a 1,2,3-triazole ring to which is attached a benzyl groups (Fig. 1).

The dihydrothiazine ring is slightly puckered as indicated by the deviations of 0.043 (2) and −0.041 (2) Å for C8 and N1, respectively, from the least-squares plane through the six atoms of this ring. The dihedral angle between this plane and that of the C1–C6 ring is 1.0 (2)°, indicating a slight twist in the dihydrobenzothiazine unit. Dihedral angles between the C1–C6 ring and, respectively, the C10–C15 and triazole rings are 0.9 (2) and 73.2 (1)° while that between the triazole and C20–C25 rings is 86.7 (2)°. The C20–C25 ring is rotationally disordered over two resolved sites with approximately equal occupancies and having the *ipso* and *para* carbon atoms (C20, C20*A*, C23, C23*A*) almost in common. The dihedral angle between the mean planes of the two components of the disorder is *ca* 59°. The packing comprises chains running parallel to the *c* axis formed by weak C19—H19*A*···O1^{i} [symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$] hydrogen bonds with the benzyl groups C19–C25 intercalated between adjacent chains (Table 1 and Fig. 2).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19*A*···O1^{i}	0.99	2.55	3.395 (4)	144

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{25}H_{20}N_4OS$
M_r	424.51
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	21.8833 (8), 5.7007 (2), 16.8054 (6)
β (°)	100.234 (1)
V (Å^3)	2063.12 (13)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.60
Crystal size (mm)	0.20 × 0.14 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.80, 0.93
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23953, 7028, 6233
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.060, 0.154, 1.10
No. of reflections	7028
No. of parameters	276
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.45

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

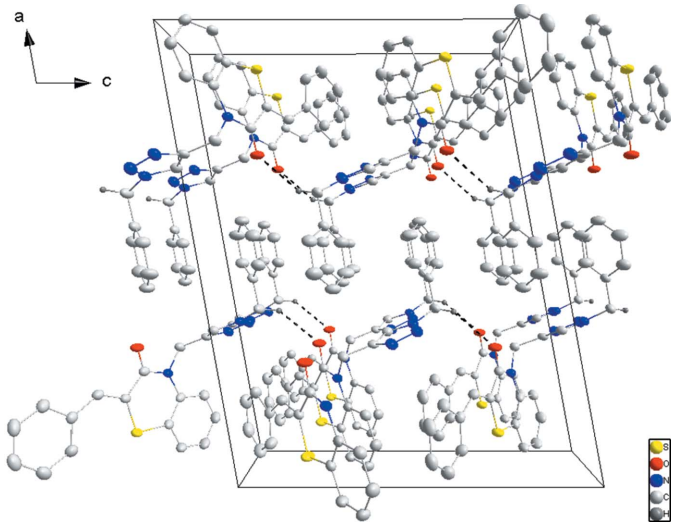


Figure 2
Packing viewed along the *b* axis with C—H···O hydrogen bonds shown as dotted lines.

Synthesis and crystallization

To a solution of 2-benzylidene-4-(prop-2-yn-1-yl)-2*H*-1,4-benzothiazin-3-one (0.2 g, 0.69 mmol) in ethanol (15 ml) was added benzyl azide (0.14 g, 1.03 mmol). The mixture was stirred under reflux for 24 h. After completion of the reaction (monitored by TLC), the solution was concentrated and the residue was purified by column chromatography on silica gel by using a 9/1 (*v*/*v*) mixture of hexane and ethyl acetate. Crystals were obtained when the solvent was allowed to evaporate. The solid product was purified by recrystallization from ethanol solution to afford green crystals in 65% yield.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The benzyl group C19–C25 is disordered over two sets of sites with approximately equal occupancies. The two components of the disorder of the benzene ring were refined as rigid hexagons. The final stages of the refinement were performed using the full, two-component, twinned data file generated by *TWINABS* (Sheldrick, 2009) since analysis of 2237 reflections having $I/\sigma(I) > 12$ and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008*a*) had shown the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *c** axis. Two reflections, *i.e.* ($\bar{1}$14) and ($\bar{1}$18), were omitted owing to poor agreement.

Acknowledgements

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References

Aloui, S., Forsal, I., Sfaira, M., Touhami, M. E., Taleb, M., Baba, M. F. & Daoudi, M. (2009). *Port. Elec. Acta*, **27**, 599–613.
Bakavoli, M., Nikpour, M., Rahimizadeh, M., Saberi, M. R. & Sadeghian, H. (2007). *Bioorg. Med. Chem.* **15**, 2120–2126.
Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2016). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Deshmukh, M. B. & Mulik, A. R. (2004). *E. J. Chem.* **1**, 206–210.
Ellouz, M., Sebbar, N. K., Essassi, E. M., Ouzidan, Y. & Mague, J. T. (2015). *Acta Cryst.* E**71**, o1022–o1023.
Fringuelli, R., Milanese, L. & Schiaffella, F. (2005). *Mini Rev. Med. Chem.* **5**, 1061–1073.
Gao, L. & Hollingsworth, R. (2005). *J. Org. Chem.* **70**, 9013–9016.
Gautam, N., Bishnoi, A. K., Guleria, A., Jangid, D. K., Gupta, S. K. & Gautam, D. C. (2013). *Heterocycl. Commun.* **19**, 37–42.
Gupta, R. & Gupta, A. (2011). *Heteroletters*, **1**, 351–358.
Kumar, M., Sharma, K., Samarth, R. M. & Kumar, A. (2010). *Eur. J. Med. Chem.* **45**, 4467–4472.
Parai, M. K. & Panda, G. A. (2009). *Tetrahedron Lett.* **50**, 4703–4705.
Podsiadły, R. (2009). *J. Photochem. Photobiol. Chem.* **202**, 115–121.
Saadouni, M., Gailane, T., Baukhris, S., Hassikou, A., Habbadi, N. & Gailane, T. (2014). *Org. Commun*, **7**, 77–84.
Sebbar, N. K., El Fal, M., Essassi, E. M., Saadi, M. & El Ammari, L. (2014). *Acta Cryst.* E**70**, o686.
Sebbar, N. K., Ellouz, M., Essassi, E. M., Ouzidan, Y. & Mague, J. T. (2015). *Acta Cryst.* E**71**, o999.
Sheldrick, G. M. (2008*a*). *CELL_NOW*. University of Göttingen, Göttingen, Germany.
Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2009). *TWINABS*. University of Göttingen, Göttingen, Germany.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Zerzouf, A., Salem, M., Essassi, E. M. & Pierrot, M. (2001). *Acta Cryst.* E**57**, o498–o499.

full crystallographic data

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Crystal data

$C_{25}H_{20}N_4OS$
M_r = 424.51
Monoclinic, $P2_1/c$
a = 21.8833 (8) Å
b = 5.7007 (2) Å
c = 16.8054 (6) Å
β = 100.234 (1)°
V = 2063.12 (13) Å^3
Z = 4
$F(000)$ = 888
D_x = 1.367 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9969 reflections
θ = 3.7–72.3°
μ = 1.60 mm^{-1}
T = 150 K
Thick plate, pale yellow
0.20 × 0.14 × 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 (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.80, T_{max} = 0.93
23953 measured reflections
7028 independent reflections
6233 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 72.4°, θ_{min} = 4.1°
h = −27→26
k = −6→6
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.154
S = 1.10
7028 reflections
276 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 2.5618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Special details

Experimental. Analysis of 2237 reflections having I/σ(I) > 12 and chosen from the full data set with*CELL_NOW* (Sheldrick, 2008*a*) showed the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *c** axis. The raw data were processed using the multi-component version of*SAINT* under control of the two-component orientation filegenerated by *CELL_NOW*.

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 benzyl group C19–C25 is disordered over two resolved sites with approximately equal occupancies. The two components of the benzene ring were refined as rigid hexagons. Refined as a 2-component twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.88790 (3)	0.42683 (15)	0.76061 (5)	0.0284 (2)	
O1	0.70554 (9)	0.3764 (4)	0.72354 (15)	0.0342 (5)	
N1	0.77326 (11)	0.1308 (4)	0.67988 (15)	0.0223 (5)	
N2	0.68783 (12)	−0.1707 (5)	0.50832 (16)	0.0297 (6)	
N3	0.66341 (13)	−0.0963 (5)	0.43493 (17)	0.0313 (6)	
N4	0.65522 (11)	0.1371 (5)	0.44063 (16)	0.0261 (6)	
C1	0.83238 (13)	0.0659 (5)	0.66352 (17)	0.0220 (6)	
C2	0.83797 (15)	−0.1250 (6)	0.61264 (19)	0.0273 (7)	
H2	0.8018	−0.2075	0.5881	0.033*	
C3	0.89534 (16)	−0.1945 (6)	0.59781 (19)	0.0326 (7)	
H3	0.8983	−0.3252	0.5637	0.039*	
C4	0.94865 (15)	−0.0745 (6)	0.6324 (2)	0.0328 (7)	
H4	0.9881	−0.1227	0.6221	0.039*	
C5	0.94397 (14)	0.1147 (6)	0.68178 (19)	0.0300 (7)	
H5	0.9803	0.1971	0.7057	0.036*	
C6	0.88592 (13)	0.1866 (5)	0.69698 (17)	0.0230 (6)	
C7	0.81087 (13)	0.4751 (5)	0.76739 (17)	0.0211 (6)	
C8	0.75995 (13)	0.3258 (5)	0.72220 (18)	0.0230 (6)	
C9	0.79322 (14)	0.6470 (5)	0.81425 (18)	0.0247 (6)	
H9	0.7498	0.6536	0.8141	0.030*	
C10	0.82944 (14)	0.8232 (5)	0.86485 (18)	0.0241 (6)	
C11	0.89435 (15)	0.8496 (6)	0.8771 (2)	0.0302 (7)	
H11	0.9186	0.7413	0.8531	0.036*	
C12	0.92330 (17)	1.0315 (6)	0.9238 (2)	0.0369 (8)	
H12	0.9672	1.0466	0.9312	0.044*	
C13	0.88953 (18)	1.1910 (6)	0.9598 (2)	0.0369 (8)	
H13	0.9098	1.3164	0.9911	0.044*	
C14	0.82594 (18)	1.1669 (7)	0.9499 (2)	0.0385 (8)	

H14	0.8024	1.2760	0.9747	0.046*	
C15	0.79610 (16)	0.9849 (6)	0.9041 (2)	0.0311 (7)	
H15	0.7524	0.9687	0.8990	0.037*	
C16	0.71955 (13)	−0.0199 (6)	0.64796 (18)	0.0249 (6)	
H16A	0.6860	0.0110	0.6791	0.030*	
H16B	0.7320	−0.1861	0.6567	0.030*	
C17	0.69457 (13)	0.0164 (5)	0.56004 (18)	0.0227 (6)	
C18	0.67379 (13)	0.2130 (6)	0.51696 (18)	0.0246 (6)	
H18	0.6727	0.3689	0.5366	0.030*	
C19	0.62386 (14)	0.2704 (7)	0.37012 (18)	0.0316 (7)	
H19A	0.6295	0.1889	0.3199	0.038*	
H19B	0.6428	0.4280	0.3701	0.038*	
C20	0.55570 (13)	0.2949 (8)	0.3717 (3)	0.0255 (7)	0.503 (3)
C21	0.52512 (18)	0.4923 (8)	0.3359 (3)	0.0379 (12)	0.503 (3)
H21	0.5475	0.6087	0.3126	0.045*	0.503 (3)
C22	0.46179 (18)	0.5194 (7)	0.3343 (3)	0.0432 (13)	0.503 (3)
H22	0.4409	0.6543	0.3099	0.052*	0.503 (3)
C23	0.42904 (13)	0.3490 (9)	0.3685 (4)	0.0393 (9)	0.503 (3)
H23	0.3858	0.3675	0.3674	0.047*	0.503 (3)
C24	0.45962 (18)	0.1516 (8)	0.4042 (3)	0.0436 (13)	0.503 (3)
H24	0.4372	0.0352	0.4276	0.052*	0.503 (3)
C25	0.52295 (18)	0.1245 (7)	0.4058 (3)	0.0350 (11)	0.503 (3)
H25	0.5439	−0.0104	0.4302	0.042*	0.503 (3)
C20A	0.55436 (12)	0.2896 (9)	0.3669 (3)	0.0255 (7)	0.497 (3)
C21A	0.53085 (17)	0.4827 (8)	0.4020 (3)	0.0379 (12)	0.497 (3)
H21A	0.5583	0.5996	0.4280	0.045*	0.497 (3)
C22A	0.46723 (19)	0.5046 (8)	0.3990 (3)	0.0432 (13)	0.497 (3)
H22A	0.4512	0.6365	0.4230	0.052*	0.497 (3)
C23A	0.42711 (13)	0.3335 (9)	0.3609 (4)	0.0393 (9)	0.497 (3)
H23A	0.3836	0.3485	0.3589	0.047*	0.497 (3)
C24A	0.45062 (17)	0.1404 (8)	0.3258 (3)	0.0436 (13)	0.497 (3)
H24A	0.4232	0.0235	0.2998	0.052*	0.497 (3)
C25A	0.51425 (19)	0.1185 (7)	0.3288 (3)	0.0350 (11)	0.497 (3)
H25A	0.5303	−0.0134	0.3048	0.042*	0.497 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0176 (3)	0.0335 (4)	0.0335 (4)	−0.0004 (3)	0.0028 (3)	−0.0095 (3)
O1	0.0164 (10)	0.0406 (14)	0.0449 (14)	0.0019 (9)	0.0033 (9)	−0.0071 (11)
N1	0.0181 (11)	0.0242 (13)	0.0236 (12)	−0.0010 (10)	0.0010 (9)	−0.0008 (10)
N2	0.0276 (14)	0.0271 (15)	0.0320 (14)	0.0011 (11)	−0.0009 (11)	−0.0045 (11)
N3	0.0310 (14)	0.0301 (15)	0.0308 (14)	0.0022 (11)	−0.0001 (11)	−0.0032 (12)
N4	0.0201 (12)	0.0288 (14)	0.0281 (13)	0.0005 (10)	0.0006 (10)	0.0033 (11)
C1	0.0204 (14)	0.0265 (16)	0.0192 (13)	0.0044 (11)	0.0034 (11)	0.0052 (12)
C2	0.0269 (15)	0.0266 (17)	0.0272 (15)	0.0037 (13)	0.0012 (12)	0.0000 (13)
C3	0.0331 (17)	0.0348 (18)	0.0299 (16)	0.0095 (15)	0.0053 (13)	−0.0054 (13)
C4	0.0258 (16)	0.041 (2)	0.0323 (17)	0.0106 (14)	0.0066 (13)	−0.0033 (15)

C5	0.0201 (14)	0.042 (2)	0.0271 (16)	0.0026 (13)	0.0023 (12)	−0.0024 (14)
C6	0.0218 (14)	0.0279 (16)	0.0186 (13)	0.0041 (12)	0.0016 (11)	0.0018 (11)
C7	0.0183 (13)	0.0239 (15)	0.0203 (14)	0.0004 (11)	0.0013 (10)	0.0027 (11)
C8	0.0203 (14)	0.0253 (16)	0.0230 (14)	0.0004 (11)	0.0024 (11)	0.0035 (12)
C9	0.0214 (14)	0.0251 (16)	0.0277 (15)	0.0020 (12)	0.0046 (11)	0.0019 (12)
C10	0.0280 (15)	0.0217 (16)	0.0231 (14)	0.0011 (12)	0.0061 (12)	0.0024 (11)
C11	0.0294 (16)	0.0286 (17)	0.0343 (17)	−0.0034 (13)	0.0101 (13)	−0.0036 (14)
C12	0.0386 (18)	0.035 (2)	0.0363 (18)	−0.0125 (15)	0.0044 (14)	−0.0010 (15)
C13	0.054 (2)	0.0260 (18)	0.0285 (16)	−0.0072 (16)	0.0007 (15)	−0.0017 (13)
C14	0.052 (2)	0.032 (2)	0.0304 (17)	0.0071 (16)	0.0044 (15)	−0.0067 (14)
C15	0.0323 (17)	0.0309 (18)	0.0302 (16)	0.0061 (13)	0.0054 (13)	−0.0014 (14)
C16	0.0220 (14)	0.0253 (16)	0.0264 (15)	−0.0041 (12)	0.0017 (11)	0.0019 (12)
C17	0.0150 (13)	0.0235 (15)	0.0285 (15)	−0.0015 (11)	0.0005 (11)	−0.0024 (12)
C18	0.0208 (14)	0.0236 (16)	0.0289 (15)	−0.0014 (11)	0.0027 (11)	−0.0020 (12)
C19	0.0228 (15)	0.043 (2)	0.0274 (15)	0.0015 (14)	0.0005 (12)	0.0090 (15)
C20	0.0208 (14)	0.0297 (17)	0.0242 (15)	0.0009 (12)	−0.0006 (11)	0.0024 (13)
C21	0.029 (2)	0.038 (3)	0.045 (3)	−0.004 (2)	0.002 (2)	−0.002 (3)
C22	0.032 (3)	0.041 (3)	0.055 (3)	0.006 (2)	0.005 (3)	−0.008 (3)
C23	0.0213 (16)	0.045 (2)	0.051 (2)	0.0018 (15)	0.0041 (15)	−0.0034 (18)
C24	0.025 (2)	0.042 (3)	0.062 (3)	−0.007 (2)	0.004 (2)	−0.003 (3)
C25	0.026 (2)	0.032 (3)	0.046 (3)	0.0020 (19)	0.003 (2)	0.000 (2)
C20A	0.0208 (14)	0.0297 (17)	0.0242 (15)	0.0009 (12)	−0.0006 (11)	0.0024 (13)
C21A	0.029 (2)	0.038 (3)	0.045 (3)	−0.004 (2)	0.002 (2)	−0.002 (3)
C22A	0.032 (3)	0.041 (3)	0.055 (3)	0.006 (2)	0.005 (3)	−0.008 (3)
C23A	0.0213 (16)	0.045 (2)	0.051 (2)	0.0018 (15)	0.0041 (15)	−0.0034 (18)
C24A	0.025 (2)	0.042 (3)	0.062 (3)	−0.007 (2)	0.004 (2)	−0.003 (3)
C25A	0.026 (2)	0.032 (3)	0.046 (3)	0.0020 (19)	0.003 (2)	0.000 (2)

Geometric parameters (Å, º)

S1—C7	1.732 (3)	C14—H14	0.9500
S1—C6	1.733 (3)	C15—H15	0.9500
O1—C8	1.229 (4)	C16—C17	1.496 (4)
N1—C8	1.378 (4)	C16—H16A	0.9900
N1—C1	1.419 (4)	C16—H16B	0.9900
N1—C16	1.478 (4)	C17—C18	1.367 (4)
N2—N3	1.324 (4)	C18—H18	0.9500
N2—C17	1.367 (4)	C19—C20	1.503 (4)
N3—N4	1.348 (4)	C19—C20A	1.516 (4)
N4—C18	1.346 (4)	C19—H19A	0.9900
N4—C19	1.471 (4)	C19—H19B	0.9900
C1—C6	1.389 (4)	C20—C21	1.3900
C1—C2	1.402 (4)	C20—C25	1.3900
C2—C3	1.381 (5)	C21—C22	1.3900
C2—H2	0.9500	C21—H21	0.9500
C3—C4	1.388 (5)	C22—C23	1.3900
C3—H3	0.9500	C22—H22	0.9500
C4—C5	1.376 (5)	C23—C24	1.3900

C4—H4	0.9500	C23—H23	0.9500
C5—C6	1.401 (4)	C24—C25	1.3900
C5—H5	0.9500	C24—H24	0.9500
C7—C9	1.356 (4)	C25—H25	0.9500
C7—C8	1.497 (4)	C20A—C21A	1.3900
C9—C10	1.456 (4)	C20A—C25A	1.3900
C9—H9	0.9500	C21A—C22A	1.3900
C10—C11	1.407 (4)	C21A—H21A	0.9500
C10—C15	1.410 (4)	C22A—C23A	1.3900
C11—C12	1.384 (5)	C22A—H22A	0.9500
C11—H11	0.9500	C23A—C24A	1.3900
C12—C13	1.377 (5)	C23A—H23A	0.9500
C12—H12	0.9500	C24A—C25A	1.3900
C13—C14	1.379 (5)	C24A—H24A	0.9500
C13—H13	0.9500	C25A—H25A	0.9500
C14—C15	1.384 (5)		

C7—S1—C6	104.38 (14)	N1—C16—H16A	108.8
C8—N1—C1	126.5 (2)	C17—C16—H16A	108.8
C8—N1—C16	115.4 (2)	N1—C16—H16B	108.8
C1—N1—C16	118.1 (3)	C17—C16—H16B	108.8
N3—N2—C17	108.8 (3)	H16A—C16—H16B	107.7
N2—N3—N4	106.7 (3)	N2—C17—C18	108.3 (3)
C18—N4—N3	111.3 (3)	N2—C17—C16	120.0 (3)
C18—N4—C19	128.3 (3)	C18—C17—C16	131.7 (3)
N3—N4—C19	120.1 (3)	N4—C18—C17	104.9 (3)
C6—C1—C2	118.2 (3)	N4—C18—H18	127.6
C6—C1—N1	121.7 (3)	C17—C18—H18	127.6
C2—C1—N1	120.1 (3)	N4—C19—C20	110.9 (3)
C3—C2—C1	120.9 (3)	N4—C19—C20A	112.8 (3)
C3—C2—H2	119.6	N4—C19—H19A	109.5
C1—C2—H2	119.6	C20—C19—H19A	109.5
C2—C3—C4	120.4 (3)	N4—C19—H19B	109.5
C2—C3—H3	119.8	C20—C19—H19B	109.5
C4—C3—H3	119.8	H19A—C19—H19B	108.1
C5—C4—C3	119.5 (3)	C21—C20—C25	120.0
C5—C4—H4	120.3	C21—C20—C19	118.1 (3)
C3—C4—H4	120.3	C25—C20—C19	121.9 (3)
C4—C5—C6	120.4 (3)	C22—C21—C20	120.0
C4—C5—H5	119.8	C22—C21—H21	120.0
C6—C5—H5	119.8	C20—C21—H21	120.0
C1—C6—C5	120.5 (3)	C21—C22—C23	120.0
C1—C6—S1	124.6 (2)	C21—C22—H22	120.0
C5—C6—S1	114.8 (2)	C23—C22—H22	120.0
C9—C7—C8	116.3 (3)	C24—C23—C22	120.0
C9—C7—S1	122.3 (2)	C24—C23—H23	120.0
C8—C7—S1	121.4 (2)	C22—C23—H23	120.0
O1—C8—N1	119.5 (3)	C25—C24—C23	120.0

O1—C8—C7	119.6 (3)	C25—C24—H24	120.0
N1—C8—C7	120.9 (2)	C23—C24—H24	120.0
C7—C9—C10	131.0 (3)	C24—C25—C20	120.0
C7—C9—H9	114.5	C24—C25—H25	120.0
C10—C9—H9	114.5	C20—C25—H25	120.0
C11—C10—C15	117.0 (3)	C21A—C20A—C25A	120.0
C11—C10—C9	126.2 (3)	C21A—C20A—C19	119.1 (3)
C15—C10—C9	116.8 (3)	C25A—C20A—C19	120.9 (3)
C12—C11—C10	120.8 (3)	C20A—C21A—C22A	120.0
C12—C11—H11	119.6	C20A—C21A—H21A	120.0
C10—C11—H11	119.6	C22A—C21A—H21A	120.0
C13—C12—C11	121.1 (3)	C23A—C22A—C21A	120.0
C13—C12—H12	119.5	C23A—C22A—H22A	120.0
C11—C12—H12	119.5	C21A—C22A—H22A	120.0
C12—C13—C14	119.3 (3)	C22A—C23A—C24A	120.0
C12—C13—H13	120.3	C22A—C23A—H23A	120.0
C14—C13—H13	120.3	C24A—C23A—H23A	120.0
C13—C14—C15	120.5 (3)	C25A—C24A—C23A	120.0
C13—C14—H14	119.7	C25A—C24A—H24A	120.0
C15—C14—H14	119.7	C23A—C24A—H24A	120.0
C14—C15—C10	121.2 (3)	C24A—C25A—C20A	120.0
C14—C15—H15	119.4	C24A—C25A—H25A	120.0
C10—C15—H15	119.4	C20A—C25A—H25A	120.0
N1—C16—C17	113.9 (2)		

C17—N2—N3—N4	0.3 (3)	C12—C13—C14—C15	−0.2 (5)
N2—N3—N4—C18	−0.4 (3)	C13—C14—C15—C10	−1.6 (5)
N2—N3—N4—C19	−175.0 (3)	C11—C10—C15—C14	2.6 (5)
C8—N1—C1—C6	6.7 (4)	C9—C10—C15—C14	−176.4 (3)
C16—N1—C1—C6	−174.5 (3)	C8—N1—C16—C17	100.5 (3)
C8—N1—C1—C2	−173.5 (3)	C1—N1—C16—C17	−78.5 (3)
C16—N1—C1—C2	5.3 (4)	N3—N2—C17—C18	−0.2 (3)
C6—C1—C2—C3	1.6 (4)	N3—N2—C17—C16	178.1 (3)
N1—C1—C2—C3	−178.2 (3)	N1—C16—C17—N2	126.5 (3)
C1—C2—C3—C4	−0.7 (5)	N1—C16—C17—C18	−55.6 (4)
C2—C3—C4—C5	0.0 (5)	N3—N4—C18—C17	0.2 (3)
C3—C4—C5—C6	−0.2 (5)	C19—N4—C18—C17	174.3 (3)
C2—C1—C6—C5	−1.7 (4)	N2—C17—C18—N4	0.0 (3)
N1—C1—C6—C5	178.1 (3)	C16—C17—C18—N4	−178.1 (3)
C2—C1—C6—S1	179.7 (2)	C18—N4—C19—C20	−79.4 (4)
N1—C1—C6—S1	−0.5 (4)	N3—N4—C19—C20	94.2 (4)
C4—C5—C6—C1	1.0 (5)	C18—N4—C19—C20A	−82.2 (4)
C4—C5—C6—S1	179.8 (3)	N3—N4—C19—C20A	91.4 (4)
C7—S1—C6—C1	−1.7 (3)	N4—C19—C20—C21	150.6 (3)
C7—S1—C6—C5	179.6 (2)	N4—C19—C20—C25	−30.9 (5)
C6—S1—C7—C9	178.1 (3)	C25—C20—C21—C22	0.0
C6—S1—C7—C8	−1.1 (3)	C19—C20—C21—C22	178.5 (5)
C1—N1—C8—O1	171.2 (3)	C20—C21—C22—C23	0.0

C16—N1—C8—O1	−7.7 (4)	C21—C22—C23—C24	0.0
C1—N1—C8—C7	−9.6 (4)	C22—C23—C24—C25	0.0
C16—N1—C8—C7	171.5 (3)	C23—C24—C25—C20	0.0
C9—C7—C8—O1	6.3 (4)	C21—C20—C25—C24	0.0
S1—C7—C8—O1	−174.4 (2)	C19—C20—C25—C24	−178.5 (5)
C9—C7—C8—N1	−172.9 (3)	N4—C19—C20A—C21A	92.4 (4)
S1—C7—C8—N1	6.3 (4)	N4—C19—C20A—C25A	−88.2 (4)
C8—C7—C9—C10	−179.2 (3)	C25A—C20A—C21A—C22A	0.0
S1—C7—C9—C10	1.5 (5)	C19—C20A—C21A—C22A	179.4 (5)
C7—C9—C10—C11	−1.3 (5)	C20A—C21A—C22A—C23A	0.0
C7—C9—C10—C15	177.6 (3)	C21A—C22A—C23A—C24A	0.0
C15—C10—C11—C12	−1.9 (5)	C22A—C23A—C24A—C25A	0.0
C9—C10—C11—C12	176.9 (3)	C23A—C24A—C25A—C20A	0.0
C10—C11—C12—C13	0.3 (5)	C21A—C20A—C25A—C24A	0.0
C11—C12—C13—C14	0.9 (5)	C19—C20A—C25A—C24A	−179.4 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19*A*···O1^{i}	0.99	2.55	3.395 (4)	144

Symmetry code: (i) $x, -y+1/2, z-1/2$.