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Synthesis, molecular and crystal structure of 1-(1,2-dihydrophthalazin-1-ylidene)-2-[1-(thiophen-2-yl)ethylidene]hydrazine

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Keywords: 2-Acetylthiophene-1-phthalazinylhydrazone; bifurcated stacking interactions; tetramers; condensation reaction; co-planar rings; chevron-shaped motifs; C—H$\cdots\pi$ interactions; crystal structure.

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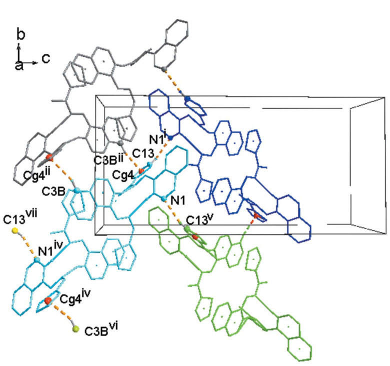
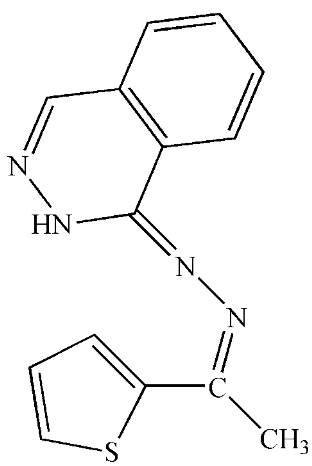
The title compound, $C_{14}H_{12}N_4S$, was synthesized by the condensation reaction of hydralazine and 2-acetylthiophene and during the reaction, a proton transfer from the imino nitrogen atom to one of the endocylic nitrogen atoms occurred. The compound crystallizes in the monoclinic crystal system with two independent molecules (molecules 1 and 2) in the asymmetric unit. In each molecule, there is a slight difference in the orientation of the thiophene ring with respect to phthalazine ring system, molecule 1 showing a dihedral angle of 42.51 (1)° compared to 8.48 (1)° in molecule 2. This implies an r.m.s deviation of 0.428 (1) Å between the two molecules for the 19 non-H atoms. The two independent molecules are connected *via* two N—H$\cdots$N hydrogen bonds, forming dimers which interact by two bifurcated π–π stacking interactions to build tetrameric motifs. The latter are packed in the *ac* plane *via* weak C—H$\cdots\pi$ interactions and along the *b* axis *via* C—H$\cdots$N and C—H$\cdots\pi$ interactions. This results a three-dimensional architecture with a tilted herringbone packing mode.



1. Chemical context

Hydralazine compounds are being studied intensively for their biological and chemical properties, the former giving them interesting pharmacological properties (antimicrobial, antimalarial and antitumor activity; Jackson *et al.*, 1990; Zelenin *et al.*, 1992; Kaminskas *et al.*, 2004; Vicini *et al.*, 2006). They also find wide applications in the treatment of tuberculosis, leprosy and mental disorder. Furthermore, there is considerable research interest in 1-hydrazinophthalazine (hydralazine) because its hydrochloride is an effective drug for the emergency reduction of blood pressure in hypertensive crises (Draey & Tripod, 1967). It has also been reported that a combination of hydralazine and hydrochlorothiazide is being used to treat high blood pressure, as they work by relaxing blood vessels and increasing the supply of blood oxygen to the heart while reducing its workload (Shoukry & Shoukry, 2008). The chemical properties of hydrazone compounds are also interesting because their nature as polydentate ligands makes them very versatile molecules. The physiological importance of hydralazine derivatives has led to great interest in their complexation tendency with metal ions, especially with transition-metal ions of biological importance. The coordination chemistry of hydrazones is being studied in connection with their increasing use as pharmaceuticals and analytical reagents. Few complexes of 1-phthalazinylhydrazone have been reported (Al'-Assar *et al.*, 1992; Kogan *et al.*, 2009; Holló *et al.*, 2014; Bakale *et al.*, 2014*b*; Levchenkov *et al.*, 2015). In a continuation of our studies of hydralazine derivatives and their complexes (Nfor *et al.*, 2013; Majoumo-Mbe *et al.*, 2015), we herein report the preparation and the structural study of the title compound, also known as 2-acetylthiophene-1-phthalazinylhydrazone.



2. Structural commentary

The title compound crystallizes in the monoclinic crystal system (space group $P2_1/n$) with two independent molecules, 1 and 2, in the asymmetric unit, as shown in Fig. 1 (atoms in molecule 2 have the suffix *B*).

There are slight differences between the molecules, as shown in Fig. 2, with an r.m.s. fit of 0.428 (1) Å for the 19 non-H atoms. This deviation arises from the different orientations of the thiophene moiety. The dihedral angle between the thiophene ring and the phthalazine ring system is 42.51 (1)° in molecule 1 compared to 8.48 (1)° in molecule 2.

In both molecules, the thiophene rings (C10–C13/S1) are in a planar conformation with a maximum deviation of 0.006 (1) Å for S1 in molecule 1 and of 0.003 (1) Å for S1*B* in molecule 2. The phthalazine ring systems are also essentially planar with maximum deviations from the best plane of the ten-membered ring systems of 0.003 (1) Å for N1 in molecule 1 and 0.022 (1) Å for C8*B* in molecule 2. The lengths of the N4—C9 and N4*B*—C9*B* bonds of 1.294 (2) and 1.296 (2) Å, respectively, are in agreement with that of an N═Csp^2 bond (1.282 ±0.060) Å found in the CSD (Version 5.39, update of August 2018; Groom *et al.*, 2016) for acyclic nitrogen and carbon atoms in organic compounds. This confirms the condensation reaction between the two reagents. The hydrogen atoms H2 and H2*B* bonded respectively to N2 and N2*B* (see Table 1) indicate that proton transfer from the imino nitrogen atoms N3 and N3*B* has occurred. The latter is confirmed by the double-bond character of N3—C8 [1.306 (2) Å] and N3*B*—C8*B* [1.309 (2) Å] and the single-bond character of N3—N4 [1.398 (2) Å] and N3*B*—N4*B* [1.400 (2) Å]. Indeed, these values are in agreement with the bond lengths for C═N and N-N bonds (1.3 ± 0.1 and 1.4 ± 0.1 Å, respectively) in the C═N—N fragment with a cyclic carbon atom and acyclic nitrogen atoms for organic compounds in the CSD. Such a proton transfer has been reported in other hydrazinophthalazine derivatives (Ianelli *et al.*, 2002; Butcher *et al.*, 2007; Popov *et al.*, 2012; Nfor *et al.*, 2013; Majoumo-Mbe *et al.*, 2015).

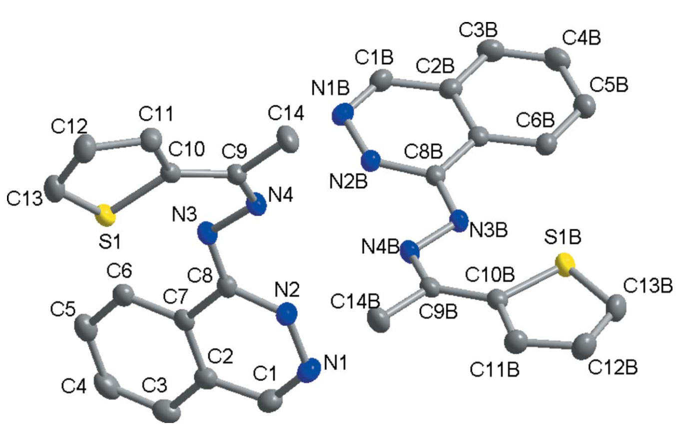


Figure 1
Molecular structure of the two independent molecules (1 and 2) with the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

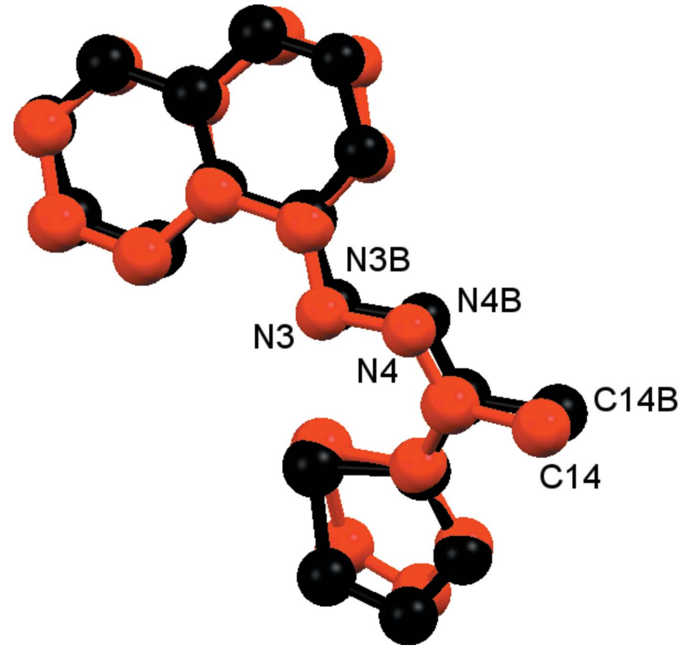


Figure 2
A view of the overlay (*Mercury*; Macrae *et al.*, 2006) of the two independent molecules (colour code: red = molecule 1, black = molecule 2).

3. Supramolecular features

Molecules 1 and 2 are linked *via* two N—H···N hydrogen bonds (see Table 1), forming dimers which are held together by two bifurcated π–π interactions (Table 1) between the phthalazine and thiophene moieties, as shown in Fig. 3. Similar bifurcated π–π interactions are also observed in 3-(benzo-

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

*Cg*1–4 are the centroids of the S1*B*/C10*B*–C13*B*, N1*B*/C1*B*/C2*B*/C7*B*/C8*B*/N2*B*, C2*B*–C7*B*, and S1/C10–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N4*B*	0.90 (2)	2.26 (2)	3.131 (2)	165 (2)
C13—H13···N1^{i}	0.94 (2)	2.61 (2)	3.387 (2)	140 (2)
N2*B*—H2*B*···N4	0.91 (2)	2.04 (2)	2.897 (2)	157 (2)
C3*B*—H3*B*···*Cg*4^{ii}	0.96 (2)	2.94 (2)	3.808 (2)	151 (2)
C11—H11···*Cg*2^{iii}	0.93 (2)	2.59 (2)	3.3796 (19)	143 (2)
*Cg*1···*Cg*2^{iv}			3.519 (2)	
*Cg*1···*Cg*3^{iv}			3.829 (2)	

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

thiazol-2-yl)thiophene (Nguyen Ngoc *et al.*, 2017). The resulting tetramers in the title compound are packed in a tilted herringbone motif. As shown in Fig. 4, they interact *via* the C13—H13···N1^{i} hydrogen bonds and C3*B*—H3*B*···*Cg*4^{ii} interactions along the *b*-axis direction (Fig. 4) and in the *ac* plane *via* C11—H11···*Cg*2^{iii} interactions (Fig. 5). The resulting packing shows small voids of 12.94 Å^3 (0.5% of the unit cell; calculated with a probe radius of 1.2 Å by using the contact surface).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, update of August 2018; Groom *et al.*, 2016) for 2-acetylthiophene-1-phthalazinylhydrazone derivatives did not give any hits. A search for structures in which the phthalazine ring exhibits bifurcated π–π interactions similar to those observed in the title structure gave six hits for organic compounds, all of which have six-membered rings: GUTYAX, GUTYOL, GUTYUR and GUTZIG (Trzesowska-Kruszynska, 2015), HILWAB (Büyükgüngör *et al.*, 2007) and TOMKIR (Bakale *et al.*, 2014*a*). None of these crystals exhibits a packing mode with a tetrameric motif similar to that reported in this work.

5. Synthesis and crystallization

The title molecule was prepared by condensation of 2-acetylthiophene (2.54 g, 20 mmol) and hydralazine hydrochloride (3.94 g, 20 mmol) in 20 ml of methanol and 10 ml of aqueous solution of sodium acetate (1.64 g, 20 mmol) as buffering agent. The mixture was refluxed at 338 K under stirring for four h. The product was left overnight to cool. The yellow precipitate was filtered off and washed several times with water and methanol, and finally crystallized from a mixture of DMF/methanol (2:1) as yellow crystals (in a yield of around 80%) suitable for single-crystal X-ray diffraction studies.

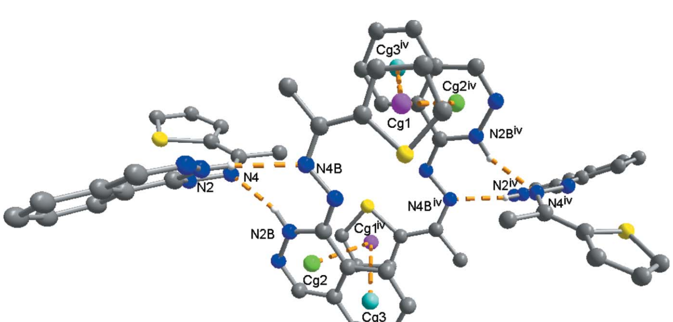


Figure 3
The packing of dimers of molecules 1 and 2 (symmetry code as in Table 1).

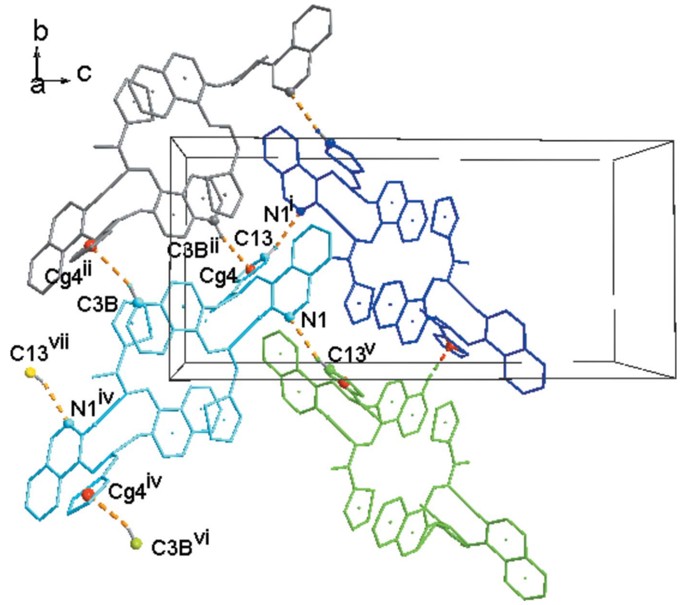


Figure 4
Packing mode of the tetramers in a herringbone motif. [Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iv) $-x+1, -y, -z$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y-1, z$; (vii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$].

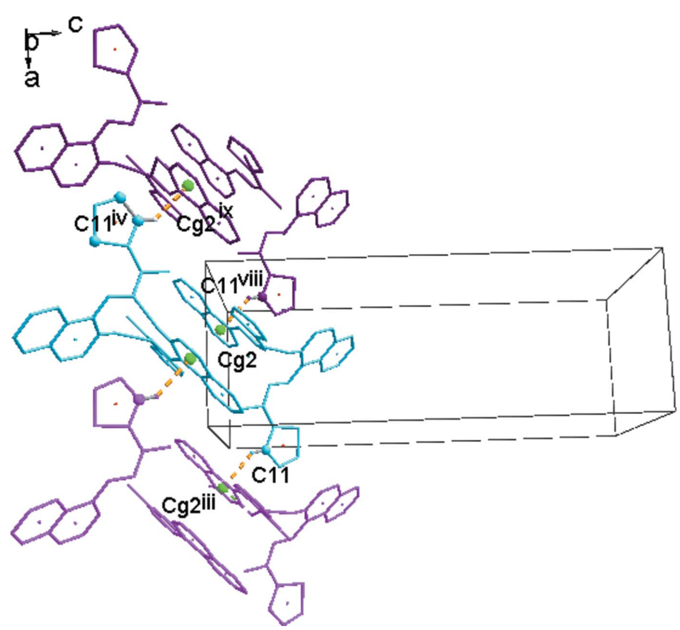


Figure 5
Packing mode of the tetramers in the *ac* plane. [Symmetry codes: (iii) $1+x, y, z$; (viii) $x-1, y, z$; (ix) $-x, -y, -z$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}N_4S$
M_r	268.34
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	130
a, *b*, *c* (Å)	8.9210 (2), 11.6792 (2), 24.7020 (4)
β (°)	90.051 (2)
V (Å^3)	2573.70 (8)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.24
Crystal size (mm)	0.2 × 0.2 × 0.1
Data collection	
Diffractometer	Agilent Xcalibur, Sapphire3, Gemini
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.995, 1
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22778, 7849, 5743
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.105, 1.02
No. of reflections	7849
No. of parameters	415
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.40

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999), *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010), *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms could be located in difference-density Fourier maps. They were refined isotropically with U_{iso}(H)= $1.2U_{eq}$(C,N).

Acknowledgements

The authors thank Dr Peter Loennecke of the University of Leipzig, Germany, for the crystal structure determination. The Cambridge Crystallographic Data Center (CCDC) is thanked for their initiative to promote structural studies in Africa and particularly in the University of Dschang (Cameroon) through the FAIRE Programme.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010), *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

1-(1,2-Dihydrophthalazin-1-ylidene)-2-[1-(thiophen-2-yl)ethylidene]hydrazine

Crystal data

$C_{14}H_{12}N_4S$
M_r = 268.34
Monoclinic, $P2_1/n$
a = 8.9210 (2) Å
b = 11.6792 (2) Å
c = 24.7020 (4) Å
β = 90.051 (2)°
V = 2573.70 (8) Å^3
Z = 8
$F(000)$ = 1120
D_x = 1.385 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5823 reflections
θ = 2.9–31.2°
μ = 0.24 mm^{-1}
T = 130 K
Prism, clear intense yellow
0.2 × 0.2 × 0.1 mm

Data collection

Agilent Xcalibur, Sapphire3, Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.356 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.995, T_{max} = 1
22778 measured reflections
7849 independent reflections
5743 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 30.5°, θ_{min} = 2.4°
h = −12→12
k = −16→14
l = −34→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.105
S = 1.02
7849 reflections
415 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.0293P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ 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.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.94607 (5)	0.48983 (4)	0.18553 (2)	0.02313 (10)
N1	0.38700 (18)	0.24390 (13)	0.23474 (6)	0.0318 (4)
N2	0.49212 (17)	0.28369 (13)	0.19925 (6)	0.0262 (3)
N3	0.66086 (16)	0.42226 (12)	0.16566 (6)	0.0230 (3)
N4	0.68717 (16)	0.34078 (12)	0.12535 (6)	0.0242 (3)
C1	0.3446 (2)	0.31335 (17)	0.27251 (8)	0.0308 (4)
C2	0.39880 (19)	0.42891 (15)	0.27863 (7)	0.0235 (3)
C3	0.3449 (2)	0.50298 (17)	0.31884 (7)	0.0294 (4)
C4	0.3953 (2)	0.61410 (17)	0.32093 (7)	0.0307 (4)
C5	0.5009 (2)	0.65325 (16)	0.28398 (8)	0.0296 (4)
C6	0.5571 (2)	0.58127 (15)	0.24471 (7)	0.0232 (3)
C7	0.50579 (18)	0.46846 (14)	0.24163 (6)	0.0199 (3)
C8	0.55718 (18)	0.38990 (14)	0.19964 (6)	0.0207 (3)
C9	0.82401 (19)	0.33588 (14)	0.10820 (6)	0.0218 (3)
C10	0.95080 (18)	0.39951 (14)	0.12963 (6)	0.0204 (3)
C11	1.0950 (2)	0.39353 (15)	0.10989 (7)	0.0256 (4)
C12	1.1994 (2)	0.45958 (16)	0.13921 (8)	0.0300 (4)
C13	1.1348 (2)	0.51514 (16)	0.18139 (8)	0.0296 (4)
C14	0.8531 (2)	0.25334 (18)	0.06250 (8)	0.0307 (4)
H2	0.512 (2)	0.2355 (18)	0.1720 (8)	0.037*
H1	0.269 (2)	0.2820 (17)	0.2976 (8)	0.037*
H3	0.274 (2)	0.4743 (17)	0.3430 (8)	0.037*
H4	0.358 (2)	0.6664 (18)	0.3478 (8)	0.037*
H5	0.535 (2)	0.7318 (18)	0.2848 (8)	0.037*
H6	0.631 (2)	0.6036 (17)	0.2200 (8)	0.037*
H11	1.119 (2)	0.3497 (18)	0.0797 (9)	0.037*
H12	1.304 (2)	0.4642 (17)	0.1304 (8)	0.037*
H13	1.178 (2)	0.5639 (18)	0.2072 (8)	0.037*
H14A	0.893 (2)	0.2920 (18)	0.0310 (9)	0.037*
H14B	0.932 (2)	0.1956 (18)	0.0732 (8)	0.037*
H14C	0.764 (2)	0.2144 (18)	0.0526 (8)	0.037*
S1B	0.36400 (5)	−0.14245 (4)	0.06118 (2)	0.02429 (10)
N1B	0.41957 (17)	0.39056 (12)	0.03070 (6)	0.0272 (3)
N2B	0.43791 (16)	0.28603 (12)	0.05466 (6)	0.0227 (3)
N3B	0.38510 (15)	0.08995 (12)	0.06759 (6)	0.0224 (3)
N4B	0.49714 (16)	0.09992 (12)	0.10701 (6)	0.0232 (3)

C1B	0.3204 (2)	0.39742 (16)	−0.00702 (7)	0.0278 (4)
C2B	0.22946 (19)	0.30252 (15)	−0.02516 (7)	0.0241 (3)
C3B	0.1233 (2)	0.31324 (17)	−0.06684 (7)	0.0308 (4)
C4B	0.0420 (2)	0.21961 (18)	−0.08347 (7)	0.0310 (4)
C5B	0.0654 (2)	0.11288 (16)	−0.05935 (7)	0.0280 (4)
C6B	0.16841 (19)	0.10032 (15)	−0.01843 (7)	0.0237 (3)
C7B	0.25136 (18)	0.19541 (14)	−0.00046 (6)	0.0208 (3)
C8B	0.36158 (18)	0.18738 (14)	0.04280 (6)	0.0203 (3)
C9B	0.54790 (18)	0.00318 (14)	0.12500 (6)	0.0215 (3)
C10B	0.49778 (18)	−0.11113 (14)	0.10992 (6)	0.0213 (3)
C11B	0.5481 (2)	−0.21069 (16)	0.13366 (7)	0.0273 (4)
C12B	0.4792 (2)	−0.31014 (17)	0.11303 (8)	0.0321 (4)
C13B	0.3777 (2)	−0.28606 (16)	0.07399 (8)	0.0302 (4)
C14B	0.6704 (2)	0.01133 (18)	0.16641 (8)	0.0287 (4)
H2B	0.512 (2)	0.2829 (17)	0.0797 (8)	0.034*
H1B	0.310 (2)	0.4713 (18)	−0.0238 (8)	0.034*
H3B	0.110 (2)	0.3875 (18)	−0.0833 (8)	0.034*
H4B	−0.029 (2)	0.2277 (17)	−0.1119 (8)	0.034*
H5B	0.008 (2)	0.0479 (18)	−0.0722 (8)	0.034*
H6B	0.184 (2)	0.0280 (18)	−0.0021 (8)	0.034*
H11B	0.623 (2)	−0.2118 (17)	0.1613 (8)	0.034*
H12B	0.499 (2)	−0.3842 (18)	0.1251 (8)	0.034*
H13B	0.318 (2)	−0.3381 (18)	0.0541 (8)	0.034*
H14D	0.639 (2)	−0.0227 (17)	0.2010 (9)	0.034*
H14E	0.696 (2)	0.0877 (18)	0.1720 (8)	0.034*
H14F	0.759 (2)	−0.0329 (17)	0.1540 (8)	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0273 (2)	0.0221 (2)	0.02000 (19)	−0.00066 (16)	−0.00166 (16)	−0.00281 (16)
N1	0.0351 (9)	0.0281 (8)	0.0324 (8)	−0.0089 (7)	0.0047 (7)	0.0011 (7)
N2	0.0319 (8)	0.0216 (7)	0.0250 (7)	−0.0041 (6)	0.0033 (6)	−0.0033 (6)
N3	0.0234 (7)	0.0238 (7)	0.0218 (7)	−0.0014 (6)	0.0006 (6)	−0.0056 (6)
N4	0.0254 (7)	0.0253 (7)	0.0219 (7)	−0.0024 (6)	0.0013 (6)	−0.0062 (6)
C1	0.0314 (10)	0.0323 (10)	0.0287 (9)	−0.0063 (8)	0.0050 (8)	0.0020 (8)
C2	0.0228 (8)	0.0265 (9)	0.0213 (8)	0.0015 (7)	−0.0024 (6)	0.0012 (7)
C3	0.0257 (9)	0.0384 (11)	0.0240 (9)	0.0051 (8)	0.0019 (7)	−0.0001 (8)
C4	0.0331 (10)	0.0342 (10)	0.0248 (9)	0.0101 (8)	−0.0035 (7)	−0.0082 (8)
C5	0.0352 (10)	0.0243 (9)	0.0293 (9)	0.0034 (8)	−0.0065 (8)	−0.0047 (8)
C6	0.0247 (8)	0.0227 (8)	0.0222 (8)	0.0002 (7)	−0.0037 (7)	0.0005 (7)
C7	0.0190 (8)	0.0229 (8)	0.0178 (7)	0.0018 (6)	−0.0038 (6)	−0.0014 (6)
C8	0.0199 (8)	0.0207 (8)	0.0214 (8)	0.0009 (6)	−0.0034 (6)	−0.0016 (6)
C9	0.0247 (8)	0.0214 (8)	0.0192 (7)	−0.0015 (6)	−0.0004 (6)	−0.0011 (6)
C10	0.0255 (8)	0.0176 (7)	0.0181 (7)	0.0008 (6)	−0.0010 (6)	0.0000 (6)
C11	0.0249 (9)	0.0249 (9)	0.0270 (9)	−0.0012 (7)	0.0024 (7)	−0.0024 (7)
C12	0.0230 (9)	0.0290 (10)	0.0380 (10)	−0.0028 (7)	−0.0013 (8)	−0.0039 (8)
C13	0.0304 (9)	0.0264 (9)	0.0319 (10)	−0.0041 (7)	−0.0070 (8)	−0.0030 (8)

C14	0.0283 (10)	0.0369 (11)	0.0271 (9)	−0.0037 (8)	0.0014 (8)	−0.0114 (8)
S1B	0.0258 (2)	0.0226 (2)	0.0244 (2)	−0.00187 (17)	−0.00405 (16)	−0.00243 (17)
N1B	0.0334 (8)	0.0215 (7)	0.0267 (7)	−0.0059 (6)	0.0031 (6)	0.0010 (6)
N2B	0.0247 (7)	0.0217 (7)	0.0217 (7)	−0.0039 (6)	−0.0014 (6)	0.0000 (6)
N3B	0.0229 (7)	0.0221 (7)	0.0223 (7)	−0.0035 (6)	−0.0045 (6)	−0.0007 (6)
N4B	0.0234 (7)	0.0246 (7)	0.0218 (7)	−0.0022 (6)	−0.0051 (6)	−0.0020 (6)
C1B	0.0344 (10)	0.0211 (8)	0.0280 (9)	−0.0034 (7)	0.0011 (8)	0.0033 (7)
C2B	0.0263 (9)	0.0243 (8)	0.0216 (8)	−0.0011 (7)	0.0021 (7)	0.0025 (7)
C3B	0.0360 (10)	0.0305 (10)	0.0260 (9)	0.0019 (8)	−0.0032 (8)	0.0075 (8)
C4B	0.0279 (9)	0.0410 (11)	0.0240 (9)	−0.0005 (8)	−0.0056 (7)	0.0032 (8)
C5B	0.0270 (9)	0.0307 (10)	0.0263 (9)	−0.0053 (7)	−0.0023 (7)	−0.0012 (8)
C6B	0.0239 (8)	0.0226 (8)	0.0245 (8)	−0.0030 (7)	0.0007 (7)	0.0002 (7)
C7B	0.0199 (8)	0.0233 (8)	0.0192 (7)	−0.0019 (6)	0.0026 (6)	−0.0013 (6)
C8B	0.0205 (8)	0.0213 (8)	0.0191 (7)	−0.0022 (6)	0.0026 (6)	−0.0016 (6)
C9B	0.0220 (8)	0.0252 (8)	0.0173 (7)	−0.0022 (6)	−0.0006 (6)	−0.0017 (6)
C10B	0.0208 (8)	0.0242 (8)	0.0190 (7)	−0.0014 (6)	0.0007 (6)	−0.0012 (6)
C11B	0.0287 (9)	0.0261 (9)	0.0271 (9)	−0.0009 (7)	−0.0034 (7)	0.0028 (7)
C12B	0.0365 (11)	0.0230 (9)	0.0369 (10)	−0.0028 (8)	−0.0015 (8)	0.0037 (8)
C13B	0.0345 (10)	0.0223 (9)	0.0337 (10)	−0.0049 (8)	−0.0016 (8)	−0.0045 (8)
C14B	0.0302 (10)	0.0305 (10)	0.0255 (9)	0.0001 (8)	−0.0082 (7)	−0.0022 (8)

Geometric parameters (Å, º)

S1—C10	1.7383 (16)	S1B—C10B	1.7336 (17)
S1—C13	1.7122 (19)	S1B—C13B	1.7112 (19)
N1—N2	1.366 (2)	N1B—N2B	1.366 (2)
N1—C1	1.293 (2)	N1B—C1B	1.287 (2)
N2—C8	1.369 (2)	N2B—C8B	1.370 (2)
N2—H2	0.90 (2)	N2B—H2B	0.91 (2)
N3—N4	1.3975 (18)	N3B—N4B	1.3996 (19)
N3—C8	1.306 (2)	N3B—C8B	1.309 (2)
N4—C9	1.294 (2)	N4B—C9B	1.296 (2)
C1—C2	1.442 (3)	C1B—C2B	1.445 (2)
C1—H1	0.99 (2)	C1B—H1B	0.96 (2)
C2—C3	1.402 (2)	C2B—C3B	1.404 (2)
C2—C7	1.400 (2)	C2B—C7B	1.405 (2)
C3—C4	1.374 (3)	C3B—C4B	1.375 (3)
C3—H3	0.93 (2)	C3B—H3B	0.96 (2)
C4—C5	1.389 (3)	C4B—C5B	1.397 (3)
C4—H4	0.96 (2)	C4B—H4B	0.95 (2)
C5—C6	1.379 (2)	C5B—C6B	1.373 (2)
C5—H5	0.97 (2)	C5B—H5B	0.97 (2)
C6—C7	1.397 (2)	C6B—C7B	1.406 (2)
C6—H6	0.93 (2)	C6B—H6B	0.95 (2)
C7—C8	1.459 (2)	C7B—C8B	1.454 (2)
C9—C10	1.453 (2)	C9B—C10B	1.456 (2)
C9—C14	1.507 (2)	C9B—C14B	1.499 (2)
C10—C11	1.378 (2)	C10B—C11B	1.377 (2)

C11—C12	1.409 (3)	C11B—C12B	1.409 (3)
C11—H11	0.93 (2)	C11B—H11B	0.96 (2)
C12—C13	1.357 (3)	C12B—C13B	1.352 (3)
C12—H12	0.96 (2)	C12B—H12B	0.93 (2)
C13—H13	0.94 (2)	C13B—H13B	0.94 (2)
C14—H14A	0.97 (2)	C14B—H14D	0.98 (2)
C14—H14B	1.01 (2)	C14B—H14E	0.93 (2)
C14—H14C	0.95 (2)	C14B—H14F	0.99 (2)
C13—S1—C10	91.87 (9)	C13B—S1B—C10B	91.68 (9)
C1—N1—N2	116.82 (15)	C1B—N1B—N2B	116.82 (15)
N1—N2—C8	126.50 (15)	N1B—N2B—C8B	126.83 (15)
N1—N2—H2	113.9 (13)	N1B—N2B—H2B	114.7 (13)
C8—N2—H2	119.4 (13)	C8B—N2B—H2B	118.4 (13)
C8—N3—N4	112.37 (14)	C8B—N3B—N4B	111.54 (13)
C9—N4—N3	115.00 (14)	C9B—N4B—N3B	114.53 (14)
N1—C1—C2	124.37 (17)	N1B—C1B—C2B	124.21 (17)
N1—C1—H1	114.9 (12)	N1B—C1B—H1B	115.9 (12)
C2—C1—H1	120.7 (12)	C2B—C1B—H1B	119.9 (12)
C3—C2—C1	122.45 (16)	C3B—C2B—C1B	122.50 (16)
C7—C2—C1	117.98 (16)	C3B—C2B—C7B	119.42 (16)
C7—C2—C3	119.54 (16)	C7B—C2B—C1B	118.07 (16)
C2—C3—H3	117.7 (13)	C2B—C3B—H3B	118.1 (12)
C4—C3—C2	119.78 (17)	C4B—C3B—C2B	120.23 (17)
C4—C3—H3	122.5 (13)	C4B—C3B—H3B	121.7 (12)
C3—C4—C5	120.53 (17)	C3B—C4B—C5B	120.24 (17)
C3—C4—H4	120.8 (13)	C3B—C4B—H4B	119.5 (12)
C5—C4—H4	118.7 (13)	C5B—C4B—H4B	120.2 (12)
C4—C5—H5	120.9 (12)	C4B—C5B—H5B	118.6 (12)
C6—C5—C4	120.59 (18)	C6B—C5B—C4B	120.59 (17)
C6—C5—H5	118.5 (12)	C6B—C5B—H5B	120.8 (12)
C5—C6—C7	119.60 (17)	C5B—C6B—C7B	119.97 (17)
C5—C6—H6	123.1 (13)	C5B—C6B—H6B	120.4 (13)
C7—C6—H6	117.3 (13)	C7B—C6B—H6B	119.6 (13)
C2—C7—C8	118.12 (15)	C2B—C7B—C6B	119.54 (16)
C6—C7—C2	119.94 (15)	C2B—C7B—C8B	118.03 (15)
C6—C7—C8	121.92 (15)	C6B—C7B—C8B	122.42 (15)
N2—C8—C7	116.19 (14)	N2B—C8B—C7B	116.01 (15)
N3—C8—N2	123.93 (15)	N3B—C8B—N2B	123.47 (15)
N3—C8—C7	119.88 (15)	N3B—C8B—C7B	120.52 (15)
N4—C9—C10	126.35 (15)	N4B—C9B—C10B	127.20 (15)
N4—C9—C14	115.90 (15)	N4B—C9B—C14B	115.65 (15)
C10—C9—C14	117.73 (15)	C10B—C9B—C14B	117.14 (15)
C9—C10—S1	125.48 (12)	C9B—C10B—S1B	125.60 (13)
C11—C10—S1	109.58 (13)	C11B—C10B—S1B	109.97 (13)
C11—C10—C9	124.89 (15)	C11B—C10B—C9B	124.41 (16)
C10—C11—C12	114.04 (16)	C10B—C11B—C12B	113.57 (17)
C10—C11—H11	121.9 (13)	C10B—C11B—H11B	122.9 (12)

C12—C11—H11	124.1 (13)	C12B—C11B—H11B	123.5 (12)
C11—C12—H12	123.9 (12)	C11B—C12B—H12B	124.4 (13)
C13—C12—C11	112.03 (17)	C13B—C12B—C11B	112.22 (17)
C13—C12—H12	124.1 (12)	C13B—C12B—H12B	123.4 (13)
S1—C13—H13	118.1 (13)	S1B—C13B—H13B	119.7 (13)
C12—C13—S1	112.47 (14)	C12B—C13B—S1B	112.55 (15)
C12—C13—H13	129.4 (13)	C12B—C13B—H13B	127.8 (13)
C9—C14—H14A	111.6 (12)	C9B—C14B—H14D	111.0 (12)
C9—C14—H14B	110.6 (12)	C9B—C14B—H14E	110.1 (13)
C9—C14—H14C	110.8 (13)	C9B—C14B—H14F	109.7 (12)
H14A—C14—H14B	105.4 (17)	H14D—C14B—H14E	109.2 (17)
H14A—C14—H14C	108.9 (18)	H14D—C14B—H14F	106.6 (16)
H14B—C14—H14C	109.3 (17)	H14E—C14B—H14F	110.1 (17)

Hydrogen-bond geometry (Å, º)

*Cg*1–4 are the centroids of the S1*B*/C10*B*–C13*B*, N1*B*/C1*B*/C2*B*/C7*B*/C8*B*/N2*B*, C2*B*–C7*B*, and S1/C10–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N4*B*	0.90 (2)	2.26 (2)	3.131 (2)	165 (2)
C13—H13···N1^{i}	0.94 (2)	2.61 (2)	3.387 (2)	140 (2)
N2*B*—H2*B*···N4	0.91 (2)	2.04 (2)	2.897 (2)	157 (2)
C3*B*—H3*B*···*Cg*4^{ii}	0.96 (2)	2.94 (2)	3.808 (2)	151 (2)
C11—H11···*Cg*2^{iii}	0.93 (2)	2.59 (2)	3.3796 (19)	143 (2)
*Cg*1···*Cg*2^{iv}			3.519 (2)	
*Cg*1···*Cg*3^{iv}			3.829 (2)	

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