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Crystal structure and Hirshfeld surface analysis of 3-benzyl-2-[bis(1*H*-pyrrol-2-yl)methyl]thiophene

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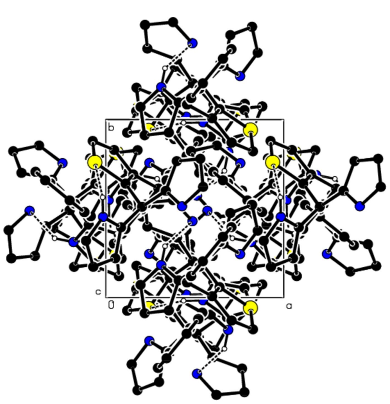
In the title compound, $C_{20}H_{18}N_2S$, the asymmetric unit comprises two similar molecules (*A* and *B*). In molecule *A*, the central thiophene ring makes dihedral angles of 89.96 (12) and 57.39 (13)° with the 1*H*-pyrrole rings, which are bent at 83.22 (14)° relative to each other, and makes an angle of 85.98 (11)° with the phenyl ring. In molecule *B*, the corresponding dihedral angles are 89.49 (13), 54.64 (12)°, 83.62 (14)° and 85.67 (11)°, respectively. In the crystal, molecular pairs are bonded to each other by N—H···N interactions. N—H···π and C—H···π interactions further connect the molecules, forming a three-dimensional network. A Hirshfeld surface analysis indicates that H···H (57.1% for molecule *A*; 57.3% for molecule *B*), C···H/H···C (30.7% for molecules *A* and *B*) and S···H/H···S (6.2% for molecule *A*; 6.4% for molecule *B*) interactions are the most important contributors to the crystal packing.



1. Chemical context

Dipyrromethanes (Nascimento *et al.*, 2019) are well-known synthetic scaffolds for the synthesis of porphyrins (Lindsey, 2010; Yedukondalu, *et al.*, 2011), calixpyrroles (Gale *et al.*, 2001) and chlorins (Taniguchi *et al.*, 2017), corroles (Orłowski *et al.*, 2017). Other important uses of dipyrromethanes include the synthesis of dipyrromethines and their complexes (Safavora *et al.*, 2019; Wood *et al.*, 2007), as fluorescent markers or in coordination compounds, including borondipyrromethenes, known as BODIPYs. The synthesis of dipyrromethanes is generally based on the acid-catalyzed condensation of pyrrole with aldehydes or acylchlorides in an organic solvent. Despite the large number of examples of the synthesis of dipyrromethanes, there is a lack of literature data on the synthesis of thiophene-substituted dipyrromethanes. Therefore, we used 3-benzylthiophenecarboxaldehyde (Zaytsev *et al.*, 2023), which, when reacted with pyrrole, gives the target dipyrromethane **1** in 70% yield (Fig. 1). On the other hand, attachment of a thiophene or pyrrole moiety to the organic molecules can lead to various sorts of intermolecular noncovalent interactions, resulting in interesting coordination, catalytic supramolecular, and solvatochromic properties (Gurbanov *et al.*, 2020*a*,*b*;Khalilov *et al.*, 2021; Mahmoudi *et al.*, 2017*a*,*b*; Mahmudov *et al.*, 2015). For example, attachment of a pyrrole moiety to ligands can create additional coordination sites and interesting supramolecular architectures,

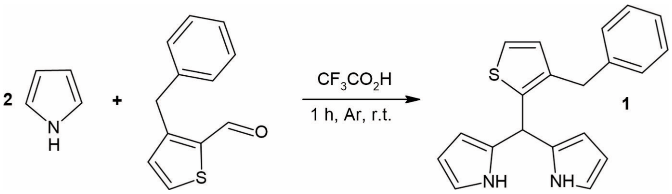
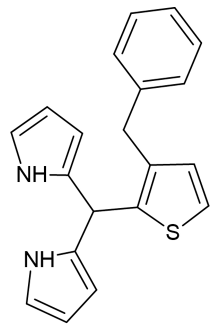


Figure 1
Synthesis of 3-benzyl-2-[bis(1*H*-pyrrol-2-yl)methyl]thiophene (**1**).

which may affect their catalytic activity (Gurbanov *et al.*, 2022*a*,*b*; Ma *et al.*, 2017, 2021; Shikhaliyev *et al.*, 2019).



2. Structural commentary

As shown Fig. 2, the title compound crystallizes with two independent molecules (*A* with the atom S1 and *B* with the atom S2) in the asymmetric unit. In molecule *A*, the central thiophene ring (S1/C2–C5) makes dihedral angles of 89.96 (12) and 57.39 (13)°, respectively, with the 1*H*-pyrrole rings (N1/C13–C16 and N2/C17–C20), which are bent at 83.22 (14)° relative to each other, and makes an angle of 85.98 (11)° with the phenyl ring (C7–C12). In molecule *B*, the central thiophene ring (S2/C22–C25) makes dihedral angles of 89.49 (13) and 54.64 (12)°, respectively, with the 1*H*-pyrrole rings (N3/C33–C36 and N4/C37–C40), which are bent at 83.62 (14)° relative to each other, and makes an angle of 85.67 (11)° with the phenyl ring (C27–C32). There is a weak intermolecular N4—H4*N*···S2 interaction (Table 1) in molecule *B*. Fig. 3 shows the overlay of molecules *A* and *B* in the asymmetric unit (r.m.s. deviation 0.055 Å). Bond lengths and angles in the molecules of the title compound are comparable with those of closely related structures detailed in section 4 (*Database survey*).

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

*Cg*1–8 are the centroids of the S1/C2–C5, N1/C13–C16, N2/C17–C20, C7–C12, S2/C22–C25, N3/C33–C36, N4/C37–C40 and C27–C32 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.87 (3)	2.61 (3)	3.270 (3)	134 (3)
N4—H4*N*···S2	0.91 (3)	2.86 (3)	3.191 (2)	103 (2)
N1—H1*N*···*Cg*6	0.87 (3)	2.65 (3)	3.300 (2)	133 (3)
N2—H2*N*···*Cg*7	0.84 (3)	2.53 (3)	3.249 (2)	145 (3)
N3—H3*N*···*Cg*3	0.87 (3)	2.70 (3)	3.335 (2)	131 (3)
N4—H4*N*···*Cg*2	0.91 (3)	2.51 (3)	3.207 (2)	134 (3)
C5—H5···*Cg*8^{i}	0.95	2.98	3.931 (3)	177
C6—H6*B*···*Cg*8^{ii}	0.99	2.79	3.697 (3)	153
C10—H10···*Cg*7^{iii}	0.95	2.86	3.544 (3)	130
C11—H11···*Cg*5^{iii}	0.95	2.98	3.874 (3)	157
C25—H25···*Cg*4^{iv}	0.95	2.98	3.924 (3)	176
C26—H26*A*···*Cg*4^{v}	0.99	2.77	3.684 (3)	153
C30—H30···*Cg*3^{vi}	0.95	2.88	3.585 (3)	132
C31—H31···*Cg*1^{vi}	0.95	2.97	3.863 (3)	156

Symmetry codes: (i) $y - 1, -x + 2, z + \frac{1}{4}$; (ii) $y, -x + 1, z + \frac{1}{4}$; (iii) $y - 1, -x + 1, z + \frac{1}{4}$; (iv) $-y + 2, x + 1, z - \frac{1}{4}$; (v) $-y + 1, x, z - \frac{1}{4}$; (vi) $-y + 1, x + 1, z - \frac{1}{4}$.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecular pairs are bonded to each other by N1—H1*N*···N3 interactions (Tables 1 and 2). N—H···π and C–H···π interactions further connect the molecules, forming a

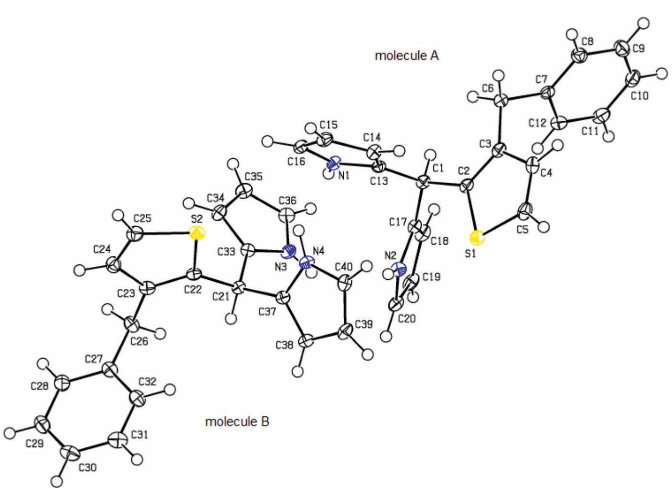


Figure 2
View of the two independent molecules, *A* and *B*, in the asymmetric unit of the title compound, with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

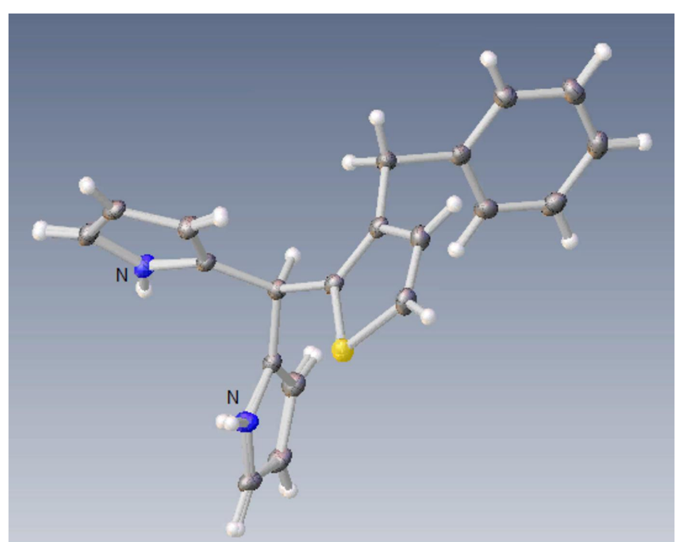


Figure 3
Overlay ball and stick image of the two independent molecules (*A* and *B*) in the asymmetric unit of the title compound. Color code: carbon (gray), hydrogen (white), nitrogen (blue) and sulfur (yellow).

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
C5···H18	3.01	$x, 1 + y, z$
H10···C40	3.01	$-1 + y, 1 - x, \frac{1}{4} + z$
H2*N*···C40	2.42	x, y, z
H4···C25	2.97	$-1 + y, 2 - x, \frac{1}{4} + z$
H1···C29	2.79	$y, 1 - x, \frac{1}{4} + z$
H15···H35	2.53	$x, 1 + y, z$
H16···H20	2.51	$1 + x, y, z$
H16···H39	2.42	$1 + x, y, z$
H19···H40	2.30	$1\ x, -1 + y, z$
H6*A*···H26*B*	2.43	$y, 2 - x, \frac{1}{4} + z$
H15···H19	2.59	$1 + x, 1 + y, z$
C25···H38	3.02	$1 + x, y, z$
H35···H20	2.42	$1 + x, y, z$
H36···H40	2.51	$x, -1 + y, z$

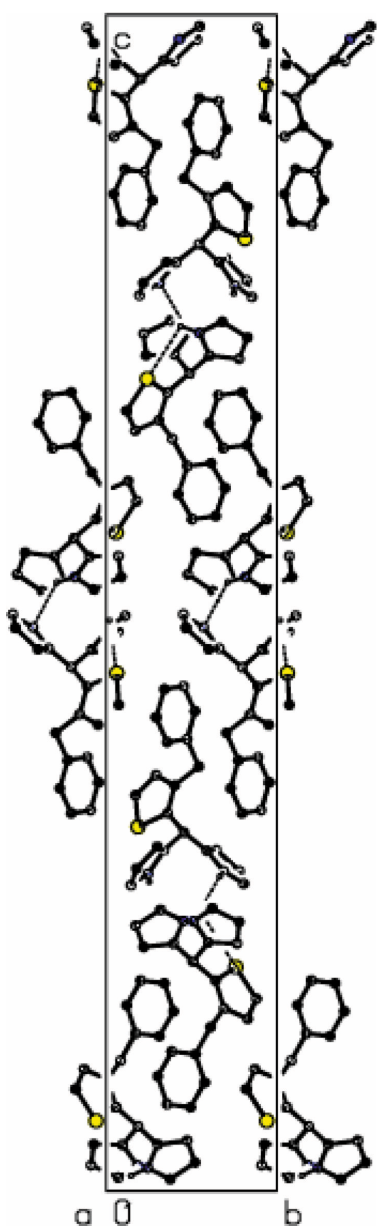


Figure 4
Packing of molecules in the title compound with the N—H···N and N—H···S hydrogen bonds, viewed along the *a* axis.

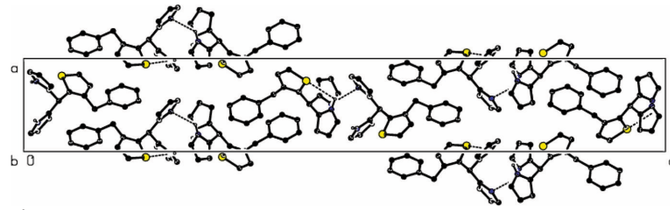


Figure 5
Packing of molecules in the title compound, viewed along the *b* axis.

three-dimensional network (Table 1; Figs, 4, 5 and 6). π-π-stacking interactions are not observed.

Crystal Explorer 17.5 (Spackman *et al.*, 2021) was used to generate Hirshfeld surfaces for both independent molecules. The $d_{\rm norm}$ mappings for molecules *A* and *B* were performed in the ranges −0.3807 to 1.3240 a.u. and −0.3811 to 1.3382 a.u., respectively. The N—H···N interactions are indicated by red areas on the Hirshfeld surfaces (Fig. 7*a*,*b* for *A* and Fig. 7*c*,*d* for *B*). Although H···H interactions (57.1% for molecule *A* and 57.3% for molecule *B*) contribute mainly to surface contacts, fingerprint plots (Fig. 8) show that C···H/H···C interactions (30.7% for molecules *A* and *B*) are also significant (Tables 1 and 2). Other, less notable contacts are S···H/H···S (6.2% for molecule *A* and 6.4% for molecule *B*), N···H/H···N (4.0% contribution for molecule *A* and 3.8% for molecule *B*), S···C/C···S (1.5% for molecule *A* and 1.3% for molecule *B*) and C···C (0.4% for molecules *A* and *B*). The comparison of the supplied data shows that molecules *A* and *B* have extremely comparable environments.

4. Database survey

Three related compounds were found in a search of the Cambridge Structural Database (CSD, version 5.42, update of

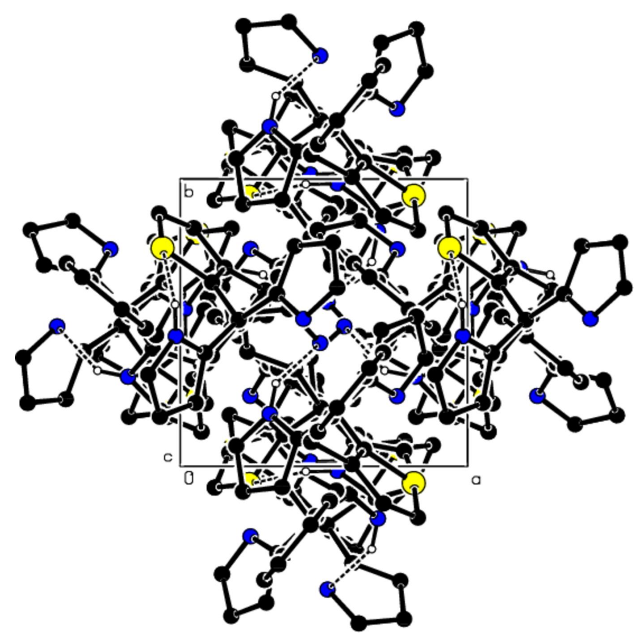


Figure 6
Packing of molecules in the title compound, viewed along the *c* axis, with interactions depicted as in Fig. 4.

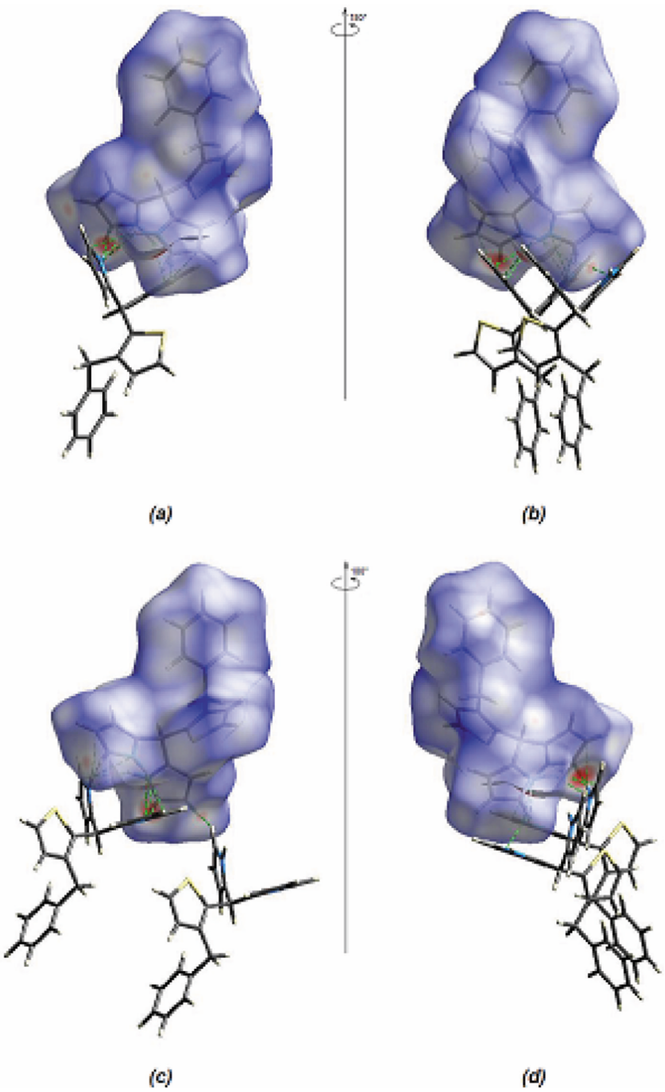


Figure 7
(*a*) Front and (*b*) back views for molecule *A*, and (*c*) front and (*d*) back views for molecule *B*, of the three-dimensional Hirshfeld surface for the title compound.

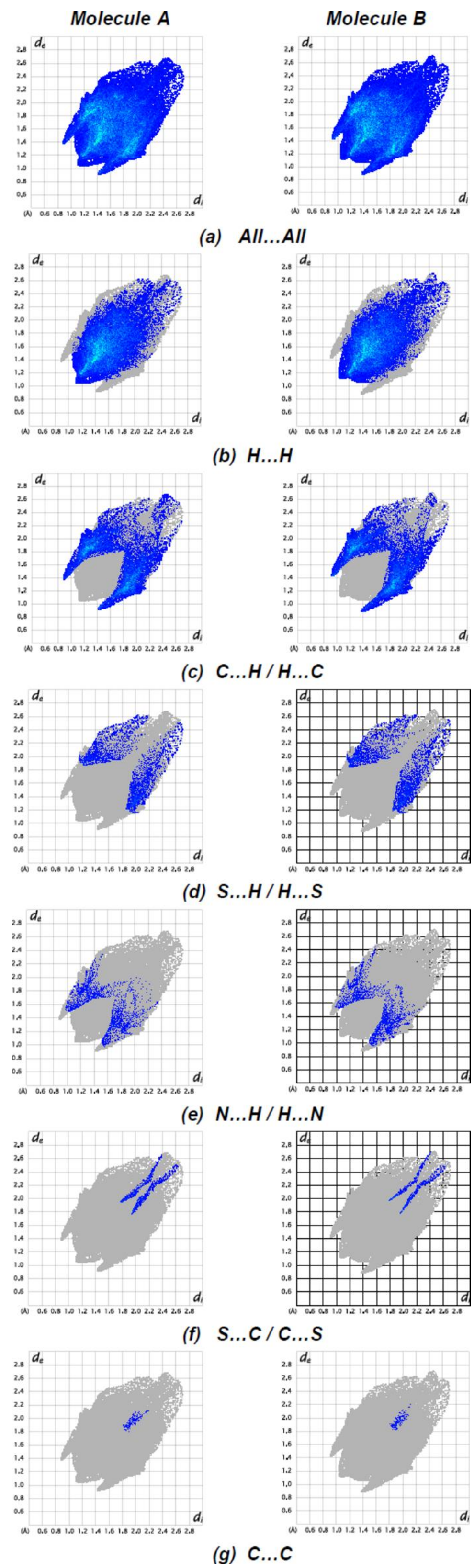


Figure 8
The two-dimensional fingerprint plots for the molecules *A* and *B* of the title compound showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C, (*d*) S···H/H···S, (*e*) N···H/H···N, (*f*) S···C/C···S and (*g*) C···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

September 2021; Groom *et al.*, 2016), *viz*. 2-amino-*N*-(2-methoxyphenyl)-4,5-dimethylthiophene-3-carboxamide (CSD refcode KODXEH; Chandra Kumar *et al.*, 2008), (2*E*)-1-(2,5-dimethyl-3-thienyl)-3-(2-methoxyphenyl)prop-2-en-1-one (SUZQUA; Asiri *et al.*, 2010*a*) and (*E*)-1-(2,5-dimethyl-3-thienyl)-3-(2-hydroxyphenyl)prop-2-en-1-one (SUYYUH; Asiri *et al.*, 2010*b*). The crystal structure of KODXEH is consolidated by both inter- and intramolecular N—H···O, C—H···O and C—H···N hydrogen bonds. In the crystal of SUZQUA, molecules are linked by weak C—H···π and aromatic π–π stacking interactions [phenyl ring centroid–centroid separation = 3.6418 (11) Å; thiophene– thiophene ring separation = 3.8727 (9) Å]. In the crystal of SUYYUH, the molecules are linked into polymeric chains extending along the *b*-axis direction by intermolecular O—H···O hydrogen bonding. An *S*(6) ring motif (Bernstein *et al.*, 1995) is formed due to a short intramolecular C—H···O contact.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{18}N_2S$
M_r	318.42
Crystal system, space group	Tetragonal, $P4_3$
Temperature (K)	100
a, c (Å)	7.74413 (3), 53.4131 (3)
V (Å^3)	3203.27 (3)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.78
Crystal size (mm)	0.18 × 0.15 × 0.12
Data collection	
Diffractometer	Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.724, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25893, 5429, 5366
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.077, 1.03
No. of reflections	5429
No. of parameters	428
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.23
Absolute structure	Flack x determined using 1866 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.003 (10)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2016/6* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

C—H···π interactions involving a methyl group of the 2,5-dimethylthienyl group and the benzene ring are present and π–π interactions between the centroids of the benzene and heterocyclic rings [3.7691 (9) Å] also occur.

5. Synthesis and crystallization

The starting 3-benzyl-2-thiophencarboxaldehyde (0.38 g, 1.88 mmol) and pyrrole (3.15 g, 47 mmol) were placed into a two-neck flask. The reaction mixture was purged with argon for 10 min. Trifluoroacetic acid (TFA, 21.4 mg, 0.19 mmol) was added dropwise to the reaction under stirring at r.t. After that, the reaction mixture was stirred for an hour under argon. Then Et_3N (50 µL) was added to pH ~7. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 10 mL). The target product was purified by column chromatography (eluent: heptane/ethyl acetate 10:1, TLC: heptane/ethyl acetate 4:1). The title compound was obtained as a yellowish powder, which quickly darkened in air, yield 70%, 0.416 g (0.132 mmol); m.p. 390 K (with decomp.). A single crystal of the title compound was grown from a mixture of heptane and ethyl acetate (~10:1). IR (KBr), ν (cm^{-1}): *br.* 3413 (NH). ^{1}H NMR (700.2 MHz, $CDCl_3$) (*J*, Hz): δ 7.80 (*br.s*, 2H, NH), 7.27 (*t*, *J* = 7.6, 2H, H Ph), 7.20 (*t*, *J* = 7.6, 1H, H Ph), 7.13 (*d*, *J* = 5.0, 1H, H Thien), 7.08 (*d*, *J* = 7.6, 2H, H Ph), 6.82 (*d*, *J* = 5.0, 1H, H Thien), 6.69–6.68 (*m*, 2H, H Pyr), 6.08 (*dd*, *J* = 5.7, *J* = 2.6, 2H, H Pyr), 6.02-6.01 (*m*, 2H, H Pyr), 5.76 (*s*, 1H, CH), 3.91 (*s*, 2H, CH_2). ^{13}C{^{1}H} NMR (176.1 MHz, $CDCl_3$): δ 140.5, 140.3, 137.0, 131.7, 129.8 (2C), 128.6 (2C), 128.5 (2C), 126.2, 123.3, 117.3 (2C), 108.5 (2C), 107.2 (2C), 37.1, 34.3. GCMS (EI, 70 eV) *m/z* (%): $[M]^+$ 318 (100), 250 (63), 239 (33), 227 (16), 184 (11), 174 (45), 91 (12). Elemental analysis calculated (%) for $C_{20}H_{18}N_2S$: C 75.44, H 5.70, N 8.80, S 10.07; found: C 75.67, H 5.41, N 9.09, S 9.81.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were included in the refinement using the riding-model approximation with C—H distances of 0.95–0.99 Å, and with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). The H atoms of the NH groups were found from a difference map and refined with U_{iso}(H) = 1.2U_{eq}(N).

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Crystal structure and Hirshfeld surface analysis of 3-benzyl-2-[bis(1*H*-pyrrol-2-yl)methyl]thiophene

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Computing details

3-Benzyl-2-[bis(1*H*-pyrrol-2-yl)methyl]thiophene

Crystal data

$C_{20}H_{18}N_2S$
M_r = 318.42
Tetragonal, $P4_3$
a = 7.74413 (3) Å
c = 53.4131 (3) Å
V = 3203.27 (3) Å^3
Z = 8
F(000) = 1344
D_x = 1.321 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 21419 reflections
θ = 3.3–79.7°
μ = 1.78 mm^{-1}
T = 100 K
Prism, yellow
0.18 × 0.15 × 0.12 mm

Data collection

Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.724, T_{max} = 1.000
25893 measured reflections
5429 independent reflections
5366 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 80.0°, θ_{min} = 3.3°
h = −9→9
k = −9→9
l = −48→67

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.03
5429 reflections
428 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
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.7104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00026 (3)
Absolute structure: Flack x determined using 1866 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.003 (10)

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	0.18679 (6)	1.05845 (6)	0.55945 (2)	0.01754 (12)
N1	0.6884 (2)	0.8179 (2)	0.52180 (4)	0.0144 (3)
H1N	0.667 (4)	0.712 (4)	0.5175 (6)	0.017*
N2	0.2448 (2)	0.7561 (2)	0.51944 (4)	0.0156 (3)
H2N	0.253 (4)	0.854 (4)	0.5127 (6)	0.019*
C1	0.4553 (3)	0.8123 (2)	0.55478 (4)	0.0142 (4)
H1	0.5195	0.7343	0.5664	0.017*
C2	0.3604 (3)	0.9414 (3)	0.57107 (4)	0.0145 (4)
C3	0.4018 (3)	0.9926 (3)	0.59474 (4)	0.0161 (4)
C4	0.2925 (3)	1.1294 (3)	0.60345 (4)	0.0191 (4)
H4	0.3031	1.1805	0.6195	0.023*
C5	0.1722 (3)	1.1786 (3)	0.58638 (5)	0.0198 (4)
H5	0.0903	1.2681	0.5890	0.024*
C6	0.5431 (3)	0.9154 (3)	0.61070 (4)	0.0176 (4)
H6A	0.6237	1.0080	0.6159	0.021*
H6B	0.6088	0.8307	0.6006	0.021*
C7	0.4729 (3)	0.8264 (3)	0.63390 (5)	0.0159 (4)
C8	0.5202 (3)	0.8793 (3)	0.65777 (5)	0.0194 (4)
H8	0.5985	0.9728	0.6597	0.023*
C9	0.4541 (3)	0.7964 (3)	0.67890 (5)	0.0224 (5)
H9	0.4865	0.8348	0.6951	0.027*
C10	0.3415 (3)	0.6587 (3)	0.67638 (5)	0.0224 (5)
H10	0.2976	0.6018	0.6908	0.027*
C11	0.2933 (3)	0.6044 (3)	0.65259 (5)	0.0225 (5)
H11	0.2159	0.5101	0.6507	0.027*
C12	0.3579 (3)	0.6878 (3)	0.63148 (5)	0.0204 (4)
H12	0.3238	0.6502	0.6153	0.024*
C13	0.5903 (2)	0.9037 (2)	0.53919 (4)	0.0134 (4)
C14	0.6455 (3)	1.0726 (3)	0.53961 (4)	0.0164 (4)
H14	0.6009	1.1623	0.5499	0.020*
C15	0.7816 (3)	1.0884 (3)	0.52183 (5)	0.0173 (4)
H15	0.8446	1.1904	0.5180	0.021*
C16	0.8047 (3)	0.9288 (3)	0.51117 (4)	0.0162 (4)
H16	0.8870	0.9004	0.4986	0.019*
C17	0.3384 (2)	0.6979 (3)	0.53944 (4)	0.0144 (4)
C18	0.2996 (3)	0.5255 (3)	0.54269 (5)	0.0180 (4)
H18	0.3461	0.4513	0.5552	0.022*
C19	0.1777 (3)	0.4791 (3)	0.52405 (5)	0.0195 (5)
H19	0.1273	0.3683	0.5217	0.023*

C20	0.1457 (3)	0.6246 (3)	0.50987 (5)	0.0178 (4)
H20	0.0692	0.6324	0.4960	0.021*
S2	0.75956 (6)	1.06184 (6)	0.44014 (2)	0.01709 (12)
N3	0.5130 (2)	0.5712 (2)	0.47912 (4)	0.0155 (3)
H3N	0.406 (4)	0.596 (4)	0.4827 (6)	0.019*
N4	0.4526 (2)	1.0157 (2)	0.47943 (4)	0.0146 (3)
H4N	0.563 (4)	1.018 (4)	0.4851 (6)	0.018*
C21	0.5097 (2)	0.7967 (2)	0.44507 (4)	0.0133 (4)
H21	0.4324	0.7315	0.4334	0.016*
C22	0.6404 (3)	0.8894 (2)	0.42877 (4)	0.0143 (4)
C23	0.6913 (3)	0.8456 (3)	0.40510 (4)	0.0155 (4)
C24	0.8293 (3)	0.9530 (3)	0.39620 (5)	0.0189 (4)
H24	0.8801	0.9410	0.3801	0.023*
C25	0.8798 (3)	1.0738 (3)	0.41317 (5)	0.0195 (4)
H25	0.9702	1.1545	0.4104	0.023*
C26	0.6123 (3)	0.7043 (3)	0.38929 (4)	0.0176 (4)
H26A	0.5272	0.6397	0.3995	0.021*
H26B	0.7039	0.6226	0.3841	0.021*
C27	0.5235 (3)	0.7752 (3)	0.36613 (4)	0.0167 (4)
C28	0.5778 (3)	0.7287 (3)	0.34221 (5)	0.0197 (4)
H28	0.6717	0.6510	0.3403	0.024*
C29	0.4953 (3)	0.7956 (3)	0.32102 (5)	0.0224 (5)
H29	0.5339	0.7635	0.3048	0.027*
C30	0.3575 (3)	0.9084 (3)	0.32360 (5)	0.0221 (5)
H30	0.3011	0.9534	0.3092	0.027*
C31	0.3025 (3)	0.9549 (3)	0.34739 (5)	0.0218 (5)
H31	0.2078	1.0318	0.3493	0.026*
C32	0.3852 (3)	0.8897 (3)	0.36853 (5)	0.0195 (4)
H32	0.3472	0.9234	0.3847	0.023*
C33	0.5996 (3)	0.6628 (3)	0.46113 (4)	0.0141 (4)
C34	0.7663 (3)	0.6010 (3)	0.46030 (5)	0.0171 (4)
H34	0.8557	0.6398	0.4495	0.021*
C35	0.7796 (3)	0.4683 (3)	0.47860 (5)	0.0177 (4)
H35	0.8798	0.4021	0.4823	0.021*
C36	0.6219 (3)	0.4531 (3)	0.48999 (4)	0.0163 (4)
H36	0.5931	0.3750	0.5030	0.020*
C37	0.3946 (3)	0.9145 (2)	0.46007 (4)	0.0140 (4)
C38	0.2205 (3)	0.9467 (3)	0.45723 (4)	0.0162 (4)
H38	0.1461	0.8951	0.4452	0.019*
C39	0.1728 (3)	1.0709 (3)	0.47547 (5)	0.0178 (4)
H39	0.0606	1.1174	0.4780	0.021*
C40	0.3186 (3)	1.1115 (3)	0.48886 (4)	0.0167 (4)
H40	0.3254	1.1917	0.5023	0.020*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0165 (2)	0.0187 (2)	0.0175 (3)	0.00554 (16)	0.00010 (19)	0.00311 (19)

N1	0.0122 (7)	0.0127 (8)	0.0183 (9)	−0.0003 (6)	0.0008 (7)	−0.0008 (7)
N2	0.0155 (8)	0.0125 (8)	0.0189 (9)	−0.0009 (6)	−0.0012 (7)	0.0011 (7)
C1	0.0134 (8)	0.0126 (8)	0.0165 (11)	0.0008 (7)	0.0005 (8)	0.0017 (8)
C2	0.0118 (8)	0.0141 (9)	0.0177 (10)	0.0003 (7)	0.0016 (8)	0.0030 (8)
C3	0.0127 (8)	0.0169 (9)	0.0188 (11)	−0.0003 (7)	0.0027 (8)	0.0018 (8)
C4	0.0197 (9)	0.0198 (10)	0.0177 (11)	0.0013 (8)	0.0047 (8)	−0.0011 (8)
C5	0.0184 (10)	0.0180 (10)	0.0230 (12)	0.0052 (7)	0.0054 (9)	0.0022 (8)
C6	0.0144 (9)	0.0226 (10)	0.0158 (10)	0.0002 (7)	0.0000 (8)	0.0011 (8)
C7	0.0115 (8)	0.0185 (9)	0.0177 (10)	0.0041 (7)	−0.0007 (7)	0.0020 (8)
C8	0.0190 (10)	0.0200 (10)	0.0192 (11)	0.0019 (8)	−0.0014 (8)	−0.0014 (8)
C9	0.0243 (11)	0.0265 (11)	0.0165 (12)	0.0062 (9)	−0.0007 (9)	0.0003 (9)
C10	0.0171 (10)	0.0274 (11)	0.0227 (12)	0.0057 (8)	0.0048 (9)	0.0062 (9)
C11	0.0149 (9)	0.0246 (11)	0.0281 (13)	0.0004 (8)	−0.0006 (9)	0.0045 (9)
C12	0.0160 (9)	0.0248 (10)	0.0203 (11)	0.0012 (8)	−0.0029 (8)	−0.0003 (9)
C13	0.0112 (8)	0.0142 (9)	0.0148 (10)	0.0012 (7)	−0.0013 (7)	−0.0003 (7)
C14	0.0155 (9)	0.0139 (9)	0.0198 (11)	−0.0003 (7)	0.0015 (8)	−0.0006 (8)
C15	0.0137 (9)	0.0167 (9)	0.0216 (12)	−0.0026 (7)	−0.0006 (8)	0.0028 (8)
C16	0.0118 (9)	0.0182 (9)	0.0187 (11)	0.0007 (7)	−0.0001 (8)	0.0021 (8)
C17	0.0128 (8)	0.0127 (9)	0.0177 (10)	0.0005 (6)	0.0023 (8)	0.0008 (7)
C18	0.0168 (9)	0.0136 (9)	0.0237 (12)	0.0014 (7)	0.0034 (8)	0.0021 (8)
C19	0.0145 (9)	0.0135 (9)	0.0305 (13)	−0.0027 (7)	0.0049 (9)	−0.0030 (9)
C20	0.0128 (9)	0.0174 (9)	0.0234 (12)	−0.0010 (7)	0.0017 (8)	−0.0036 (8)
S2	0.0176 (2)	0.0167 (2)	0.0169 (2)	−0.00542 (17)	−0.00261 (18)	−0.00039 (18)
N3	0.0128 (8)	0.0136 (8)	0.0203 (10)	−0.0009 (6)	0.0003 (7)	0.0014 (7)
N4	0.0118 (8)	0.0137 (7)	0.0184 (9)	0.0005 (6)	−0.0018 (7)	−0.0013 (7)
C21	0.0126 (8)	0.0121 (8)	0.0152 (10)	−0.0001 (7)	−0.0002 (7)	0.0002 (7)
C22	0.0132 (8)	0.0126 (8)	0.0171 (11)	0.0000 (6)	−0.0024 (8)	0.0009 (8)
C23	0.0160 (9)	0.0118 (8)	0.0185 (11)	0.0003 (7)	−0.0025 (8)	0.0018 (8)
C24	0.0202 (10)	0.0190 (10)	0.0174 (11)	−0.0002 (8)	0.0015 (8)	0.0037 (8)
C25	0.0179 (9)	0.0189 (10)	0.0216 (11)	−0.0048 (7)	−0.0009 (8)	0.0049 (8)
C26	0.0236 (10)	0.0140 (9)	0.0151 (11)	0.0003 (7)	−0.0006 (8)	−0.0006 (8)
C27	0.0204 (9)	0.0126 (9)	0.0171 (11)	−0.0038 (7)	−0.0007 (8)	−0.0002 (8)
C28	0.0201 (10)	0.0192 (10)	0.0197 (12)	−0.0020 (8)	0.0011 (8)	−0.0014 (8)
C29	0.0276 (11)	0.0232 (11)	0.0165 (11)	−0.0065 (9)	0.0008 (9)	−0.0013 (9)
C30	0.0275 (11)	0.0173 (9)	0.0214 (12)	−0.0063 (8)	−0.0076 (9)	0.0036 (9)
C31	0.0240 (11)	0.0145 (9)	0.0268 (13)	−0.0006 (8)	−0.0050 (9)	−0.0007 (8)
C32	0.0246 (10)	0.0159 (9)	0.0181 (11)	−0.0009 (8)	−0.0010 (9)	−0.0032 (8)
C33	0.0150 (9)	0.0123 (8)	0.0149 (10)	−0.0001 (7)	−0.0010 (8)	0.0003 (7)
C34	0.0145 (9)	0.0150 (9)	0.0219 (11)	0.0015 (7)	0.0028 (8)	0.0008 (8)
C35	0.0170 (9)	0.0124 (9)	0.0237 (12)	0.0028 (7)	−0.0013 (9)	−0.0005 (8)
C36	0.0184 (10)	0.0111 (8)	0.0194 (11)	−0.0012 (7)	−0.0012 (8)	0.0018 (8)
C37	0.0138 (9)	0.0126 (8)	0.0157 (10)	−0.0004 (7)	−0.0008 (7)	0.0018 (7)
C38	0.0127 (9)	0.0162 (9)	0.0196 (11)	−0.0005 (7)	−0.0015 (8)	0.0023 (8)
C39	0.0133 (9)	0.0159 (9)	0.0244 (12)	0.0021 (7)	0.0036 (8)	0.0046 (8)
C40	0.0182 (9)	0.0125 (9)	0.0194 (11)	0.0016 (7)	0.0035 (8)	−0.0003 (8)

Geometric parameters (Å, º)

S1—C5	1.717 (2)	S2—C25	1.718 (2)
S1—C2	1.736 (2)	S2—C22	1.733 (2)
N1—C16	1.368 (3)	N3—C33	1.370 (3)
N1—C13	1.371 (3)	N3—C36	1.373 (3)
N1—H1N	0.87 (3)	N3—H3N	0.87 (3)
N2—C17	1.367 (3)	N4—C40	1.372 (3)
N2—C20	1.374 (3)	N4—C37	1.373 (3)
N2—H2N	0.84 (3)	N4—H4N	0.91 (3)
C1—C17	1.508 (3)	C21—C37	1.506 (3)
C1—C13	1.513 (3)	C21—C33	1.515 (3)
C1—C2	1.516 (3)	C21—C22	1.516 (3)
C1—H1	1.0000	C21—H21	1.0000
C2—C3	1.363 (3)	C22—C23	1.367 (3)
C3—C4	1.433 (3)	C23—C24	1.435 (3)
C3—C6	1.510 (3)	C23—C26	1.511 (3)
C4—C5	1.358 (3)	C24—C25	1.360 (3)
C4—H4	0.9500	C24—H24	0.9500
C5—H5	0.9500	C25—H25	0.9500
C6—C7	1.519 (3)	C26—C27	1.518 (3)
C6—H6A	0.9900	C26—H26A	0.9900
C6—H6B	0.9900	C26—H26B	0.9900
C7—C8	1.388 (3)	C27—C28	1.392 (3)
C7—C12	1.401 (3)	C27—C32	1.397 (3)
C8—C9	1.395 (4)	C28—C29	1.399 (3)
C8—H8	0.9500	C28—H28	0.9500
C9—C10	1.384 (4)	C29—C30	1.386 (3)
C9—H9	0.9500	C29—H29	0.9500
C10—C11	1.389 (4)	C30—C31	1.388 (4)
C10—H10	0.9500	C30—H30	0.9500
C11—C12	1.392 (4)	C31—C32	1.393 (3)
C11—H11	0.9500	C31—H31	0.9500
C12—H12	0.9500	C32—H32	0.9500
C13—C14	1.376 (3)	C33—C34	1.377 (3)
C14—C15	1.424 (3)	C34—C35	1.422 (3)
C14—H14	0.9500	C34—H34	0.9500
C15—C16	1.372 (3)	C35—C36	1.370 (3)
C15—H15	0.9500	C35—H35	0.9500
C16—H16	0.9500	C36—H36	0.9500
C17—C18	1.380 (3)	C37—C38	1.380 (3)
C18—C19	1.419 (3)	C38—C39	1.418 (3)
C18—H18	0.9500	C38—H38	0.9500
C19—C20	1.380 (3)	C39—C40	1.373 (3)
C19—H19	0.9500	C39—H39	0.9500
C20—H20	0.9500	C40—H40	0.9500
C5—S1—C2	91.97 (11)	C25—S2—C22	92.07 (11)

C16—N1—C13	109.97 (17)	C33—N3—C36	109.93 (18)
C16—N1—H1N	128 (2)	C33—N3—H3N	120 (2)
C13—N1—H1N	122 (2)	C36—N3—H3N	130 (2)
C17—N2—C20	110.05 (18)	C40—N4—C37	109.73 (18)
C17—N2—H2N	126 (2)	C40—N4—H4N	125.4 (19)
C20—N2—H2N	124 (2)	C37—N4—H4N	124.8 (19)
C17—C1—C13	113.00 (18)	C37—C21—C33	112.67 (18)
C17—C1—C2	114.11 (16)	C37—C21—C22	114.41 (16)
C13—C1—C2	110.00 (16)	C33—C21—C22	110.03 (16)
C17—C1—H1	106.4	C37—C21—H21	106.4
C13—C1—H1	106.4	C33—C21—H21	106.4
C2—C1—H1	106.4	C22—C21—H21	106.4
C3—C2—C1	127.62 (18)	C23—C22—C21	127.31 (18)
C3—C2—S1	111.20 (16)	C23—C22—S2	111.21 (15)
C1—C2—S1	120.97 (17)	C21—C22—S2	121.28 (16)
C2—C3—C4	112.14 (19)	C22—C23—C24	112.16 (19)
C2—C3—C6	125.35 (19)	C22—C23—C26	125.44 (19)
C4—C3—C6	122.5 (2)	C24—C23—C26	122.4 (2)
C5—C4—C3	113.3 (2)	C25—C24—C23	113.1 (2)
C5—C4—H4	123.4	C25—C24—H24	123.5
C3—C4—H4	123.4	C23—C24—H24	123.5
C4—C5—S1	111.42 (17)	C24—C25—S2	111.47 (16)
C4—C5—H5	124.3	C24—C25—H25	124.3
S1—C5—H5	124.3	S2—C25—H25	124.3
C3—C6—C7	112.39 (17)	C23—C26—C27	112.14 (17)
C3—C6—H6A	109.1	C23—C26—H26A	109.2
C7—C6—H6A	109.1	C27—C26—H26A	109.2
C3—C6—H6B	109.1	C23—C26—H26B	109.2
C7—C6—H6B	109.1	C27—C26—H26B	109.2
H6A—C6—H6B	107.9	H26A—C26—H26B	107.9
C8—C7—C12	118.6 (2)	C28—C27—C32	118.7 (2)
C8—C7—C6	121.4 (2)	C28—C27—C26	121.2 (2)
C12—C7—C6	120.0 (2)	C32—C27—C26	120.1 (2)
C7—C8—C9	120.7 (2)	C27—C28—C29	120.6 (2)
C7—C8—H8	119.7	C27—C28—H28	119.7
C9—C8—H8	119.7	C29—C28—H28	119.7
C10—C9—C8	120.5 (2)	C30—C29—C28	120.3 (2)
C10—C9—H9	119.8	C30—C29—H29	119.9
C8—C9—H9	119.8	C28—C29—H29	119.9
C9—C10—C11	119.4 (2)	C29—C30—C31	119.4 (2)
C9—C10—H10	120.3	C29—C30—H30	120.3
C11—C10—H10	120.3	C31—C30—H30	120.3
C10—C11—C12	120.3 (2)	C30—C31—C32	120.5 (2)
C10—C11—H11	119.9	C30—C31—H31	119.8
C12—C11—H11	119.9	C32—C31—H31	119.8
C11—C12—C7	120.6 (2)	C31—C32—C27	120.6 (2)
C11—C12—H12	119.7	C31—C32—H32	119.7
C7—C12—H12	119.7	C27—C32—H32	119.7

N1—C13—C14	107.44 (18)	N3—C33—C34	107.54 (18)
N1—C13—C1	121.91 (17)	N3—C33—C21	121.77 (18)
C14—C13—C1	130.59 (19)	C34—C33—C21	130.56 (19)
C13—C14—C15	107.50 (19)	C33—C34—C35	107.30 (19)
C13—C14—H14	126.3	C33—C34—H34	126.3
C15—C14—H14	126.3	C35—C34—H34	126.3
C16—C15—C14	107.19 (19)	C36—C35—C34	107.60 (19)
C16—C15—H15	126.4	C36—C35—H35	126.2
C14—C15—H15	126.4	C34—C35—H35	126.2
N1—C16—C15	107.90 (19)	C35—C36—N3	107.62 (19)
N1—C16—H16	126.0	C35—C36—H36	126.2
C15—C16—H16	126.0	N3—C36—H36	126.2
N2—C17—C18	107.57 (19)	N4—C37—C38	107.43 (19)
N2—C17—C1	123.30 (17)	N4—C37—C21	123.56 (18)
C18—C17—C1	129.1 (2)	C38—C37—C21	129.0 (2)
C17—C18—C19	107.6 (2)	C37—C38—C39	107.6 (2)
C17—C18—H18	126.2	C37—C38—H38	126.2
C19—C18—H18	126.2	C39—C38—H38	126.2
C20—C19—C18	107.31 (19)	C40—C39—C38	107.39 (19)
C20—C19—H19	126.3	C40—C39—H39	126.3
C18—C19—H19	126.3	C38—C39—H39	126.3
N2—C20—C19	107.5 (2)	N4—C40—C39	107.89 (19)
N2—C20—H20	126.2	N4—C40—H40	126.1
C19—C20—H20	126.2	C39—C40—H40	126.1

C17—C1—C2—C3	141.6 (2)	C37—C21—C22—C23	−140.9 (2)
C13—C1—C2—C3	−90.2 (3)	C33—C21—C22—C23	91.1 (2)
C17—C1—C2—S1	−44.1 (2)	C37—C21—C22—S2	44.7 (2)
C13—C1—C2—S1	84.15 (19)	C33—C21—C22—S2	−83.3 (2)
C5—S1—C2—C3	0.81 (17)	C25—S2—C22—C23	−0.63 (17)
C5—S1—C2—C1	−174.41 (17)	C25—S2—C22—C21	174.56 (17)
C1—C2—C3—C4	174.28 (19)	C21—C22—C23—C24	−174.53 (19)
S1—C2—C3—C4	−0.5 (2)	S2—C22—C23—C24	0.3 (2)
C1—C2—C3—C6	−6.8 (3)	C21—C22—C23—C26	6.8 (3)
S1—C2—C3—C6	178.40 (16)	S2—C22—C23—C26	−178.37 (16)
C2—C3—C4—C5	−0.1 (3)	C22—C23—C24—C25	0.3 (3)
C6—C3—C4—C5	−179.1 (2)	C26—C23—C24—C25	179.0 (2)
C3—C4—C5—S1	0.7 (2)	C23—C24—C25—S2	−0.8 (2)
C2—S1—C5—C4	−0.88 (18)	C22—S2—C25—C24	0.80 (18)
C2—C3—C6—C7	−115.1 (2)	C22—C23—C26—C27	114.7 (2)
C4—C3—C6—C7	63.7 (3)	C24—C23—C26—C27	−63.9 (3)
C3—C6—C7—C8	−120.0 (2)	C23—C26—C27—C28	118.9 (2)
C3—C6—C7—C12	60.1 (3)	C23—C26—C27—C32	−60.9 (3)
C12—C7—C8—C9	−0.3 (3)	C32—C27—C28—C29	0.0 (3)
C6—C7—C8—C9	179.8 (2)	C26—C27—C28—C29	−179.7 (2)
C7—C8—C9—C10	0.7 (3)	C27—C28—C29—C30	−0.4 (3)
C8—C9—C10—C11	−0.6 (3)	C28—C29—C30—C31	0.3 (3)
C9—C10—C11—C12	0.1 (3)	C29—C30—C31—C32	0.3 (3)

C10—C11—C12—C7	0.3 (3)	C30—C31—C32—C27	−0.6 (3)
C8—C7—C12—C11	−0.3 (3)	C28—C27—C32—C31	0.5 (3)
C6—C7—C12—C11	179.67 (19)	C26—C27—C32—C31	−179.75 (19)
C16—N1—C13—C14	0.0 (2)	C36—N3—C33—C34	0.6 (2)
C16—N1—C13—C1	−177.46 (19)	C36—N3—C33—C21	176.96 (18)
C17—C1—C13—N1	−47.6 (2)	C37—C21—C33—N3	45.3 (3)
C2—C1—C13—N1	−176.43 (19)	C22—C21—C33—N3	174.30 (19)
C17—C1—C13—C14	135.5 (2)	C37—C21—C33—C34	−139.3 (2)
C2—C1—C13—C14	6.7 (3)	C22—C21—C33—C34	−10.3 (3)
N1—C13—C14—C15	0.0 (2)	N3—C33—C34—C35	−0.4 (3)
C1—C13—C14—C15	177.2 (2)	C21—C33—C34—C35	−176.2 (2)
C13—C14—C15—C16	0.0 (3)	C33—C34—C35—C36	0.0 (3)
C13—N1—C16—C15	0.0 (2)	C34—C35—C36—N3	0.4 (2)
C14—C15—C16—N1	0.0 (3)	C33—N3—C36—C35	−0.7 (2)
C20—N2—C17—C18	0.4 (2)	C40—N4—C37—C38	−0.1 (2)
C20—N2—C17—C1	−177.61 (18)	C40—N4—C37—C21	178.37 (19)
C13—C1—C17—N2	−55.8 (2)	C33—C21—C37—N4	58.7 (3)
C2—C1—C17—N2	70.8 (3)	C22—C21—C37—N4	−68.0 (3)
C13—C1—C17—C18	126.7 (2)	C33—C21—C37—C38	−123.2 (2)
C2—C1—C17—C18	−106.7 (2)	C22—C21—C37—C38	110.2 (2)
N2—C17—C18—C19	−0.3 (2)	N4—C37—C38—C39	−0.1 (2)
C1—C17—C18—C19	177.5 (2)	C21—C37—C38—C39	−178.4 (2)
C17—C18—C19—C20	0.2 (2)	C37—C38—C39—C40	0.2 (2)
C17—N2—C20—C19	−0.3 (2)	C37—N4—C40—C39	0.2 (2)
C18—C19—C20—N2	0.1 (2)	C38—C39—C40—N4	−0.2 (2)

Hydrogen-bond geometry (Å, º)

*Cg*1–8 are the centroids of the S1/C2–C5, N1/C13–C16, N2/C17–C20, C7–C12, S2/C22–C25, N3/C33–C36, N4/C37–C40 and C27–C32 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.87 (3)	2.61 (3)	3.270 (3)	134 (3)
N4—H4*N*···S2	0.91 (3)	2.86 (3)	3.191 (2)	103 (2)
N1—-H1*N*···*Cg*6	0.87 (3)	2.65 (3)	3.300 (2)	133 (3)
N2—-H2*N*···*Cg*7	0.84 (3)	2.53 (3)	3.249 (2)	145 (3)
N3—-H3*N*···*Cg*3	0.87 (3)	2.70 (3)	3.335 (2)	131 (3)
N4—-H4*N*···*Cg*2	0.91 (3)	2.51 (3)	3.207 (2)	134 (3)
C5—-H5···*Cg*8^{i}	0.95	2.98	3.931 (3)	177
C6—-H6*B*···*Cg*8^{ii}	0.99	2.79	3.697 (3)	153
C10—-H10···*Cg*7^{iii}	0.95	2.86	3.544 (3)	130
C11—-H11···*Cg*5^{iii}	0.95	2.98	3.874 (3)	157
C25—-H25···*Cg*4^{iv}	0.95	2.98	3.924 (3)	176
C26—-H26*A*···*Cg*4^{v}	0.99	2.77	3.684 (3)	153
C30—-H30···*Cg*3^{vi}	0.95	2.88	3.585 (3)	132
C31—-H31···*Cg*1^{vi}	0.95	2.97	3.863 (3)	156

Symmetry codes: (i) *y*−1, −*x*+2, *z*+1/4; (ii) *y*, −*x*+1, *z*+1/4; (iii) *y*−1, −*x*+1, *z*+1/4; (iv) −*y*+2, *x*+1, *z*−1/4; (v) −*y*+1, *x*, *z*−1/4; (vi) −*y*+1, *x*+1, *z*−1/4.