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3,3′-(Hexane-1,6-diyl)bis(1-vinyl-4-imidazoline-2-thione)

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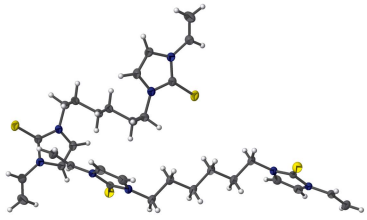
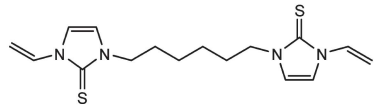
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{22}N_4S_2$, was obtained by the reaction of sulfur with the corresponding quaternary salt in the presence of K_2CO_3. It crystallizes with two half-molecules in the asymmetric unit; the complete molecules are generated by inversion symmetry with the central $CH_2—CH_2$ bonds of the hexane bridges being located on inversion centres. In each molecule, the C_6-alkyl chain adopts a typical antiperiplanar conformation and the two heterocyclic rings are oriented antiparallel to each other. In the crystal, molecules are linked by C—H$\cdots\pi$ interactions, forming layers lying parallel to the *ac* plane.

3D view



Chemical scheme



Structure description

The title compound was obtained from 3,3′-(hexane-1,6-diyl)bis(1-vinylimidazolium) dibromide (Cui *et al.*, 2014) by reaction with elemental sulfur in the presence of K_2CO_3. Imidazoline-2-thiones (Laus *et al.*, 2013) are versatile building blocks whose properties have been reviewed by Trzhtsinskaya & Abramova (1991). The crucial advantages of these thiones are simple synthesis and simple derivation in the realm of imidazole chemistry, a mainstay of ionic liquid research. A field of current relevance, poly(ionic liquids) are macromolecules derived from organic salts which are liquid below 373 K (Yuan & Antonietti, 2011). The vinyl substituent renders the title molecule polymerizable, and the bidentate nature of the molecule facilitates cross-linking, thus giving access to a plethora of functionalized imidazolium-containing polymers (Anderson & Long, 2010). They in turn offer a multitude of applications and represent major advances in materials science.

The unit cell contains two independent half-molecules (Fig. 1), which are completed by inversion symmetry. The centres of symmetry lie at the mid-point of the $(CH_2)_6$ spacer

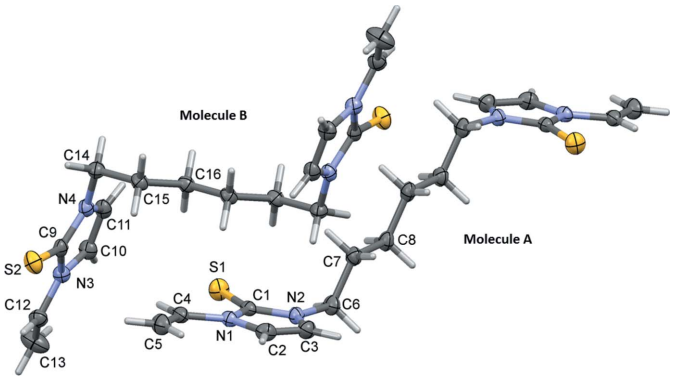


Figure 1
A view of the molecular structure of the two independent molecules (*A* and *B*) of the title compound, with atom labelling. The displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related to the labelled atoms by symmetry operations ($-x+1, -y+1, -z+2$) for molecule *A* and ($-x, -y+1, -z+1$) for molecule *B*.

between the two imidazoline-2-thione rings. As in other bridged bis(imidazoline-2-thiones), the C_6-alkyl chain adopts a typical antiperiplanar conformation (Bhabak *et al.*, 2011; Beheshti *et al.*, 2016), and the two heterocyclic rings are oriented antiparallel to each other, as can be seen in Fig. 1. The lengths of the C=S bonds are 1.680 (1) and 1.682 (1) Å, in perfect accordance with the mean value (Laus *et al.*, 2013) in the Cambridge Structural Database (Groom *et al.*, 2016). Related structures have been reported with short methylene or ethylene bridges (Liu *et al.*, 2003; Jia *et al.*, 2008), C_3-to-C_5 bridges (Bhabak *et al.*, 2011; Beheshti *et al.*, 2016), and longer linkers (Marshall *et al.*, 2005; Marshall & Harrison, 2007).

In the crystal, molecules are linked by C—H···π interactions, forming layers lying parallel to the *ac* plane (Table 1 and Fig. 2).

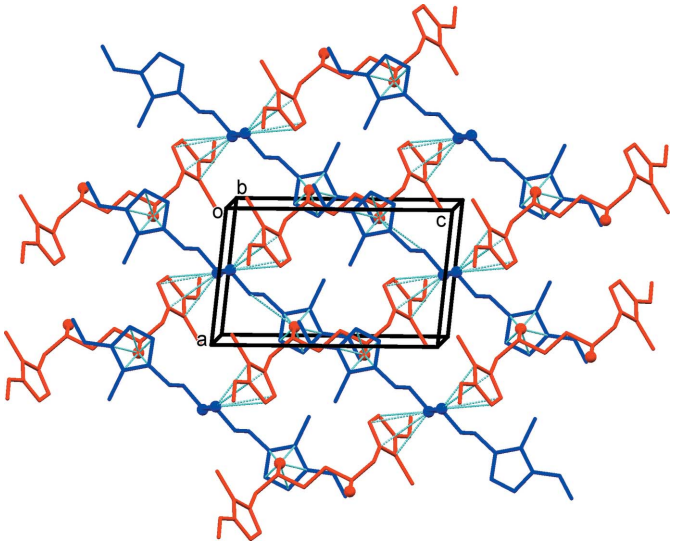


Figure 2
A view along the *b* axis of the crystal packing of the title compound, (colour code: blue *A* molecules, red *B* molecules). The C—H···π interactions are shown as dashed lines, and only H atoms H8*B* and H15*B* (blue and red balls, respectively) have been included.

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

*Cg*1 and *Cg*2 are the centroids of the N1/N2/C1–C3 and N3/N4/C9–C11 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···*Cg*2^{i}	0.99	2.75	3.628 (2)	148
C15—H15*B*···*Cg*1^{ii}	0.99	2.76	3.589 (2)	142

Symmetry codes: (i) $x, y, z+1$; (ii) $-x, -y+1, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{22}N_4S_2$
M_r	334.5
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, *b*, *c* (Å)	7.1335 (5), 10.6863 (5), 11.8830 (6)
α, β, γ (°)	99.856 (4), 93.530 (5), 101.937 (5)
V (Å^3)	868.75 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.31
Crystal size (mm)	0.54 × 0.2 × 0.14
Data collection	
Diffractometer	Agilent Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.880, 1
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5545, 3151, 2821
R_{int}	0.013
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.029, 0.072, 1.05
No. of reflections	3151
No. of parameters	199
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.20

Computer programs: (*CrysAlis PRO*; Agilent, 2014), *SIR2002* (Burla *et al.*, 2003), *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Synthesis and crystallization

A mixture of 3,3′-(hexane-1,6-diyl)bis(1-vinylimidazolium) dibromide (55.6 g, 129 mmol), sulfur (8.25 g, 257 mmol) and K_2CO_3 (35.6 g, 257 mmol) in MeOH (200 ml) was refluxed for 3 h. After evaporation of the solvent under reduced pressure, the residue was extracted with hot $CHCl_3$ (3 × 250 ml), followed by hot filtration and evaporation of the solvent. To the residue, EtOH (200 ml) was added and the mixture was ultrasonicated for 30 min. The product was collected by filtration and dried in high vacuum for 24 h (yield 40.0 g, 93%; m.p. 423 K). Single crystals were obtained by slow evaporation of a $CHCl_3$ solution. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (*m*, 4H), 1.68 (*m*, 4H), 3.92 (*t*, *J* = 7.4 Hz, 4H), 4.80 (*dd*, *J* = 9.0, 1.8 Hz, 2H), 5.05 (*dd*, *J* = 16.1, 1.8 Hz, 2H), 6.68 (*d*, *J* = 2.6 Hz, 2H), 6.91 (*d*, *J* = 2.6 Hz, 2H), 7.44 (*dd*, *J* = 16.1, 9.0 Hz, 2H) p.p.m. ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 28.2, 47.2, 100.6, 112.4, 118.1, 130.0, 162.3 p.p.m. IR (neat): ν 3126, 3092, 2943,

2855, 1639, 1454, 1421, 1401, 1363, 1288, 1259, 1233, 1160, 975, 875, 831, 762, 742, 718, 697, 659, 518, 486 cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2017). **2**, x170599 [https://doi.org/10.1107/S2414314617005995]

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Crystal data

$C_{16}H_{22}N_4S_2$
M_r = 334.5
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.1335 (5) Å
b = 10.6863 (5) Å
c = 11.8830 (6) Å
α = 99.856 (4)°
β = 93.530 (5)°
γ = 101.937 (5)°
V = 868.75 (9) Å^3
Z = 2
$F(000)$ = 356
D_x = 1.279 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3343 reflections
θ = 4.0–28.5°
μ = 0.31 mm^{-1}
T = 173 K
Prismatic fragment, colourless
0.54 × 0.2 × 0.14 mm

Data collection

Agilent Xcalibur Ruby Gemini ultra diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.3575 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.880, T_{max} = 1
5545 measured reflections
3151 independent reflections
2821 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.4°, θ_{min} = 3.5°
h = −6→8
k = −12→11
l = −14→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.072
S = 1.05
3151 reflections
199 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.3242P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.42181 (5)	0.23294 (4)	0.56557 (3)	0.03198 (11)
S2	−0.05723 (5)	0.23677 (4)	0.07703 (3)	0.03264 (11)
N4	0.22259 (16)	0.40254 (11)	0.23089 (10)	0.0230 (3)
N3	0.28775 (16)	0.21338 (11)	0.17699 (10)	0.0234 (3)
N2	0.16867 (17)	0.19534 (11)	0.72562 (10)	0.0237 (3)
N1	0.02845 (16)	0.16137 (10)	0.55287 (10)	0.0216 (2)
C1	0.20569 (19)	0.19571 (12)	0.61534 (11)	0.0212 (3)
C14	0.1222 (2)	0.50945 (14)	0.24615 (12)	0.0270 (3)
H14A	0.0525	0.5112	0.172	0.032*
H14B	0.2178	0.593	0.2699	0.032*
C9	0.15171 (19)	0.28462 (13)	0.16221 (11)	0.0231 (3)
C7	0.3279 (2)	0.37721 (14)	0.87953 (12)	0.0268 (3)
H7A	0.2061	0.3851	0.9129	0.032*
H7B	0.3436	0.4314	0.8195	0.032*
C8	0.4943 (2)	0.42931 (14)	0.97290 (12)	0.0269 (3)
H8A	0.6164	0.422	0.9397	0.032*
H8B	0.479	0.3754	1.0331	0.032*
C11	0.3978 (2)	0.40436 (14)	0.28805 (12)	0.0263 (3)
H11	0.475	0.4756	0.3414	0.032*
C10	0.4393 (2)	0.28843 (14)	0.25507 (12)	0.0268 (3)
H10	0.5515	0.262	0.2802	0.032*
C15	−0.0198 (2)	0.49571 (14)	0.33577 (12)	0.0252 (3)
H15A	−0.1108	0.41	0.3133	0.03*
H15B	−0.0952	0.5638	0.3362	0.03*
C12	0.2730 (2)	0.08475 (14)	0.11905 (13)	0.0279 (3)
H12	0.1562	0.0426	0.0729	0.033*
C13	0.4068 (3)	0.01920 (17)	0.12376 (17)	0.0465 (5)
H13A	0.5258	0.0579	0.169	0.056*
H13B	0.3857	−0.0675	0.082	0.056*
C16	0.07338 (19)	0.50680 (13)	0.45661 (12)	0.0240 (3)
H16A	0.1478	0.4383	0.457	0.029*
H16B	0.1645	0.5924	0.4796	0.029*
C6	0.3136 (2)	0.23646 (14)	0.82447 (12)	0.0292 (3)
H6A	0.4403	0.2258	0.7997	0.035*
H6B	0.2797	0.1803	0.8817	0.035*
C5	−0.1648 (2)	0.12107 (15)	0.37121 (14)	0.0354 (4)
H5A	−0.2801	0.1019	0.407	0.042*
H5B	−0.1707	0.1173	0.2906	0.042*
C3	−0.0276 (2)	0.16310 (14)	0.73221 (13)	0.0287 (3)
H3	−0.0894	0.1575	0.8003	0.034*

C2	−0.1148 (2)	0.14119 (14)	0.62602 (13)	0.0275 (3)
H2	−0.2497	0.1164	0.6044	0.033*
C4	0.0022 (2)	0.15270 (13)	0.43297 (12)	0.0260 (3)
H4	0.1142	0.1712	0.3941	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02078 (19)	0.0399 (2)	0.0333 (2)	0.00365 (15)	0.00389 (15)	0.00479 (17)
S2	0.0251 (2)	0.0409 (2)	0.0281 (2)	0.00743 (16)	−0.00448 (15)	−0.00125 (16)
N4	0.0222 (6)	0.0255 (6)	0.0207 (6)	0.0046 (5)	0.0047 (5)	0.0026 (5)
N3	0.0205 (6)	0.0255 (6)	0.0233 (6)	0.0037 (5)	0.0020 (5)	0.0037 (5)
N2	0.0252 (6)	0.0235 (6)	0.0210 (6)	0.0047 (5)	−0.0004 (5)	0.0025 (5)
N1	0.0202 (6)	0.0207 (6)	0.0229 (6)	0.0043 (4)	−0.0004 (5)	0.0027 (4)
C1	0.0229 (7)	0.0174 (6)	0.0227 (7)	0.0053 (5)	−0.0008 (5)	0.0018 (5)
C14	0.0310 (8)	0.0257 (7)	0.0262 (7)	0.0091 (6)	0.0047 (6)	0.0059 (6)
C9	0.0224 (7)	0.0277 (7)	0.0194 (7)	0.0041 (6)	0.0060 (5)	0.0052 (5)
C7	0.0282 (7)	0.0297 (8)	0.0209 (7)	0.0040 (6)	−0.0020 (6)	0.0048 (6)
C8	0.0273 (7)	0.0335 (8)	0.0188 (7)	0.0041 (6)	−0.0005 (6)	0.0059 (6)
C11	0.0217 (7)	0.0307 (8)	0.0227 (7)	0.0000 (6)	0.0014 (6)	0.0023 (6)
C10	0.0212 (7)	0.0310 (8)	0.0265 (8)	0.0038 (6)	−0.0011 (6)	0.0045 (6)
C15	0.0248 (7)	0.0248 (7)	0.0265 (7)	0.0084 (6)	0.0035 (6)	0.0020 (6)
C12	0.0269 (8)	0.0253 (7)	0.0289 (8)	0.0019 (6)	0.0024 (6)	0.0029 (6)
C13	0.0357 (9)	0.0348 (9)	0.0623 (12)	0.0109 (7)	−0.0056 (8)	−0.0091 (8)
C16	0.0218 (7)	0.0231 (7)	0.0262 (7)	0.0056 (5)	0.0035 (6)	0.0016 (6)
C6	0.0327 (8)	0.0325 (8)	0.0219 (7)	0.0077 (6)	−0.0047 (6)	0.0053 (6)
C5	0.0386 (9)	0.0352 (8)	0.0305 (8)	0.0084 (7)	−0.0077 (7)	0.0045 (7)
C3	0.0280 (8)	0.0278 (7)	0.0303 (8)	0.0044 (6)	0.0078 (6)	0.0058 (6)
C2	0.0198 (7)	0.0268 (7)	0.0350 (8)	0.0038 (6)	0.0035 (6)	0.0044 (6)
C4	0.0316 (8)	0.0219 (7)	0.0237 (7)	0.0066 (6)	−0.0004 (6)	0.0024 (6)

Geometric parameters (Å, º)

S1—C1	1.6805 (14)	C8—H8B	0.99
S2—C9	1.6820 (14)	C11—C10	1.333 (2)
N4—C9	1.3576 (18)	C11—H11	0.95
N4—C11	1.3799 (18)	C10—H10	0.95
N4—C14	1.4609 (18)	C15—C16	1.5196 (19)
N3—C9	1.3721 (18)	C15—H15A	0.99
N3—C10	1.3914 (18)	C15—H15B	0.99
N3—C12	1.4078 (18)	C12—C13	1.299 (2)
N2—C1	1.3531 (18)	C12—H12	0.95
N2—C3	1.3812 (18)	C13—H13A	0.95
N2—C6	1.4585 (18)	C13—H13B	0.95
N1—C1	1.3724 (17)	C16—C16^{ii}	1.517 (3)
N1—C2	1.3889 (18)	C16—H16A	0.99
N1—C4	1.4101 (18)	C16—H16B	0.99
C14—C15	1.5188 (19)	C6—H6A	0.99

C14—H14A	0.99	C6—H6B	0.99
C14—H14B	0.99	C5—C4	1.309 (2)
C7—C6	1.514 (2)	C5—H5A	0.95
C7—C8	1.5178 (19)	C5—H5B	0.95
C7—H7A	0.99	C3—C2	1.333 (2)
C7—H7B	0.99	C3—H3	0.95
C8—C8^{i}	1.521 (3)	C2—H2	0.95
C8—H8A	0.99	C4—H4	0.95

C9—N4—C11	110.30 (12)	C11—C10—N3	107.23 (13)
C9—N4—C14	124.54 (12)	C11—C10—H10	126.4
C11—N4—C14	125.10 (12)	N3—C10—H10	126.4
C9—N3—C10	109.60 (12)	C14—C15—C16	114.16 (12)
C9—N3—C12	123.89 (12)	C14—C15—H15A	108.7
C10—N3—C12	126.51 (12)	C16—C15—H15A	108.7
C1—N2—C3	110.19 (12)	C14—C15—H15B	108.7
C1—N2—C6	124.83 (12)	C16—C15—H15B	108.7
C3—N2—C6	124.68 (12)	H15A—C15—H15B	107.6
C1—N1—C2	109.63 (11)	C13—C12—N3	125.10 (14)
C1—N1—C4	123.53 (12)	C13—C12—H12	117.4
C2—N1—C4	126.82 (12)	N3—C12—H12	117.4
N2—C1—N1	105.20 (11)	C12—C13—H13A	120
N2—C1—S1	127.50 (10)	C12—C13—H13B	120
N1—C1—S1	127.29 (10)	H13A—C13—H13B	120
N4—C14—C15	111.76 (11)	C16^{ii}—C16—C15	112.40 (14)
N4—C14—H14A	109.3	C16^{ii}—C16—H16A	109.1
C15—C14—H14A	109.3	C15—C16—H16A	109.1
N4—C14—H14B	109.3	C16^{ii}—C16—H16B	109.1
C15—C14—H14B	109.3	C15—C16—H16B	109.1
H14A—C14—H14B	107.9	H16A—C16—H16B	107.9
N4—C9—N3	105.07 (12)	N2—C6—C7	111.33 (12)
N4—C9—S2	127.37 (11)	N2—C6—H6A	109.4
N3—C9—S2	127.56 (11)	C7—C6—H6A	109.4
C6—C7—C8	113.07 (12)	N2—C6—H6B	109.4
C6—C7—H7A	109	C7—C6—H6B	109.4
C8—C7—H7A	109	H6A—C6—H6B	108
C6—C7—H7B	109	C4—C5—H5A	120
C8—C7—H7B	109	C4—C5—H5B	120
H7A—C7—H7B	107.8	H5A—C5—H5B	120
C7—C8—C8^{i}	112.14 (15)	C2—C3—N2	107.85 (13)
C7—C8—H8A	109.2	C2—C3—H3	126.1
C8^{i}—C8—H8A	109.2	N2—C3—H3	126.1
C7—C8—H8B	109.2	C3—C2—N1	107.13 (12)
C8^{i}—C8—H8B	109.2	C3—C2—H2	126.4
H8A—C8—H8B	107.9	N1—C2—H2	126.4
C10—C11—N4	107.79 (12)	C5—C4—N1	124.94 (14)
C10—C11—H11	126.1	C5—C4—H4	117.5
N4—C11—H11	126.1	N1—C4—H4	117.5

C3—N2—C1—N1	−0.75 (15)	C9—N4—C11—C10	0.59 (15)
C6—N2—C1—N1	−174.72 (12)	C14—N4—C11—C10	177.66 (12)
C3—N2—C1—S1	178.20 (10)	N4—C11—C10—N3	−0.32 (15)
C6—N2—C1—S1	4.2 (2)	C9—N3—C10—C11	−0.04 (16)
C2—N1—C1—N2	0.35 (14)	C12—N3—C10—C11	178.96 (13)
C4—N1—C1—N2	178.70 (11)	N4—C14—C15—C16	65.34 (16)
C2—N1—C1—S1	−178.60 (10)	C9—N3—C12—C13	173.65 (16)
C4—N1—C1—S1	−0.25 (19)	C10—N3—C12—C13	−5.2 (2)
C9—N4—C14—C15	83.69 (16)	C14—C15—C16—C16^{ii}	179.71 (14)
C11—N4—C14—C15	−92.97 (15)	C1—N2—C6—C7	95.37 (16)
C11—N4—C9—N3	−0.59 (14)	C3—N2—C6—C7	−77.73 (17)
C14—N4—C9—N3	−177.68 (11)	C8—C7—C6—N2	−172.50 (12)
C11—N4—C9—S2	179.67 (10)	C1—N2—C3—C2	0.89 (16)
C14—N4—C9—S2	2.58 (19)	C6—N2—C3—C2	174.87 (13)
C10—N3—C9—N4	0.39 (14)	N2—C3—C2—N1	−0.64 (16)
C12—N3—C9—N4	−178.64 (12)	C1—N1—C2—C3	0.18 (15)
C10—N3—C9—S2	−179.88 (10)	C4—N1—C2—C3	−178.10 (13)
C12—N3—C9—S2	1.09 (19)	C1—N1—C4—C5	−179.54 (14)
C6—C7—C8—C8^{i}	−179.90 (15)	C2—N1—C4—C5	−1.5 (2)

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

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the N1/N2/C1–C3 and N3/N4/C9–C11 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···*Cg*2^{iii}	0.99	2.75	3.628 (2)	148
C15—H15*B*···*Cg*1^{ii}	0.99	2.76	3.589 (2)	142

Symmetry codes: (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*, *y*, *z*+1.