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# A second polymorph of 3,4-bis(6-bromopyridin-3-yl)-1,2,5-thiadiazole

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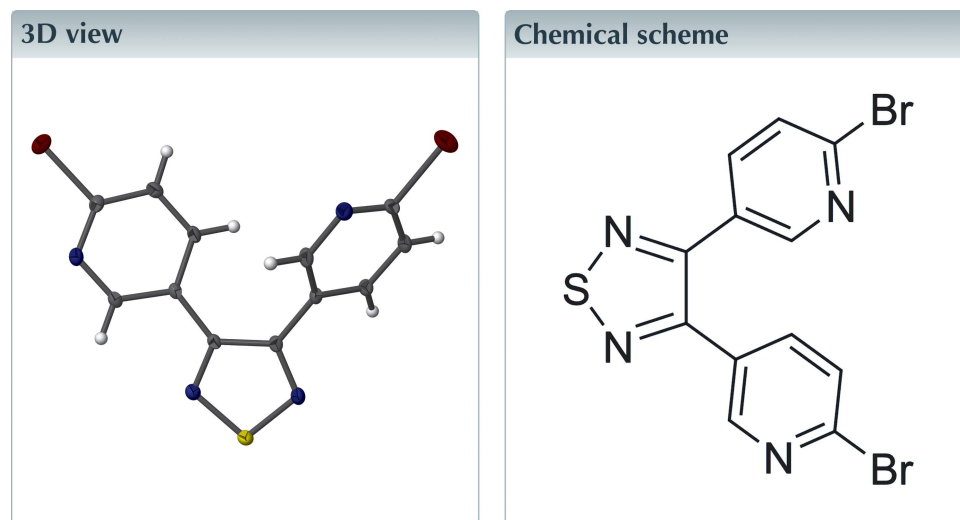
Edited by H. Ishida, Okayama University, Japan

Keywords: crystal structure; heterocycle; thiadiazole; polymorph.

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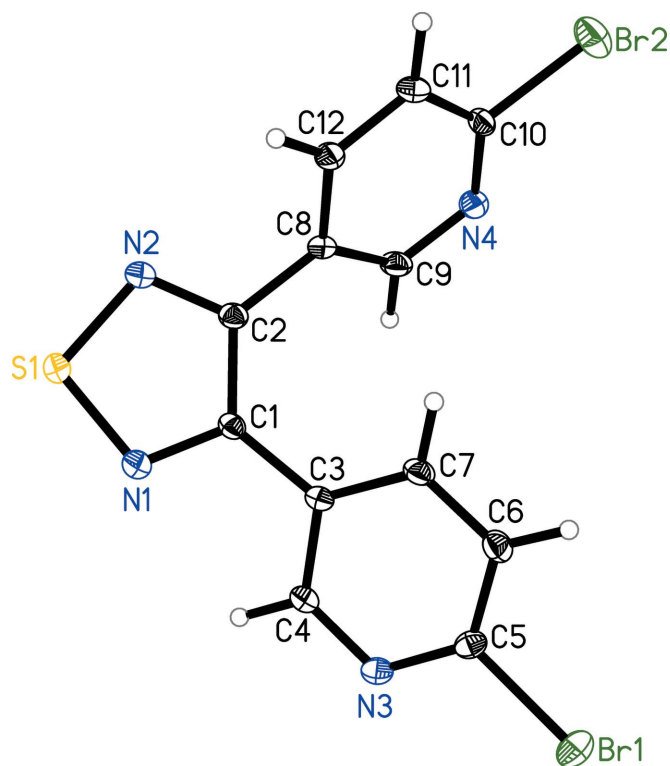
Structural data: full structural data are available from iucrdata.iucr.org

The title compound,  $C_{12}H_6Br_2N_4S$ , a second polymorph in the triclinic space group  $P\bar{1}$ , is presented. As in the earlier reported monoclinic polymorph in the space group  $C2/c$  [Becker *et al.* (2016). *Chem. Eur. J.* In the press], the thiadiazole ring is planar with an r.m.s. deviation of 0.004 Å. The five-membered ring is tilted with respect to the two pyridyl substituents by 23.16 (7) and 49.47 (9)°. In the crystal, molecules are linked by a weak non-bonding  $Br \cdots N$  interaction [3.056 (3) Å]. Furthermore, a column of molecules is established along the  $b$  axis by  $\pi$ - $\pi$  stacking interactions between the pyridine rings [centroid-centroid distances = 3.7014 (16) and 3.5934 (15) Å]. Additionally, a short intermolecular  $Br \cdots Br$  contact [3.3791 (6) Å] and  $Br \cdots \pi$ -aryl contacts [3.6815 (11)–3.7659 (12) Å] towards the thiadiazole and pyridine rings are found.

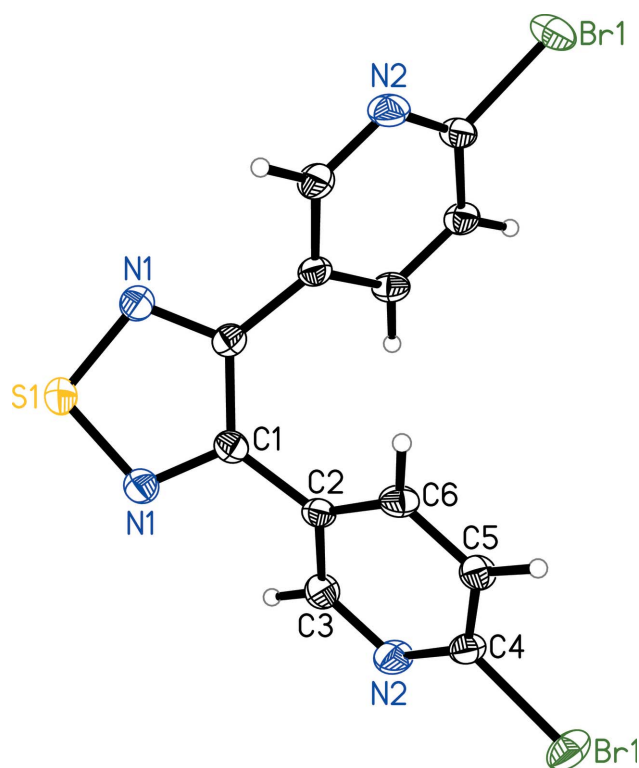


## Structure description

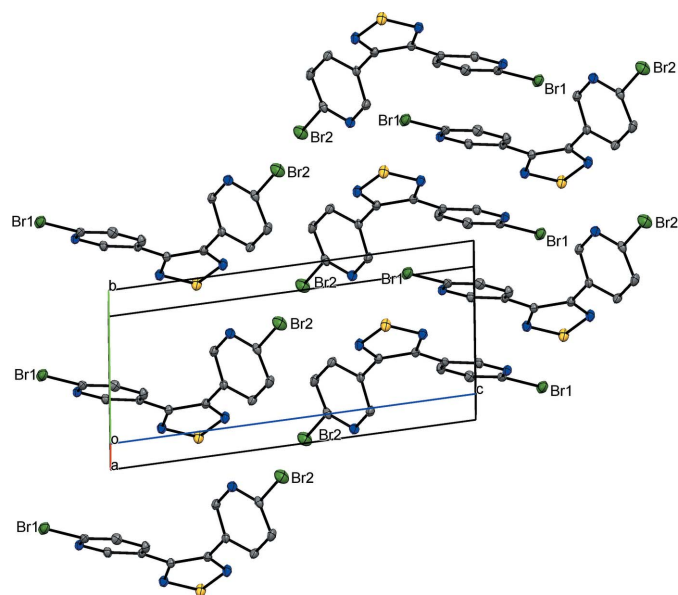
The title compound was formed by the reaction of  $SOCl_2$  with  $[Ti(C_5Me_5)_2(N=C(R)-C(R)=N)]$  ( $R = 6\text{-Br-3-py}$ ), as the coupling product of two molecules of 2-bromo-5-cyanopyridine at  $[Ti(C_5Me_5)_2]$  (Becker *et al.*, 2016). Triclinic ( $P\bar{1}$ ) and monoclinic ( $C2/c$ ) polymorphs of the title compound were observed, the triclinic one being presented here (Fig. 1). The thiadiazole ring is planar (*r.m.s.* deviation 0.004 Å) as found in the earlier reported monoclinic polymorph. This fact and the N–S [N1–S1 1.625 (2), N2–S2 1.629 (2) Å], C–N [C1–N1 1.332 (3), C2–N2 1.324 (3) Å] and C–C [C1–C2 1.441 (3) Å] bond lengths indicate electron delocalization in the ring system. The five-membered S1/N1/C1/C2/N2 ring makes dihedral angles of 23.16 (7) and 49.47 (9)°, respectively, with the N3/C3–C7 and N4/C8–C12 pyridyl substituents. Examples for similar symmetrical substituted 1,2,5-thiadiazole derivatives were published by Mellini &



**Figure 1**  
Molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at the 50% probability level.



**Figure 2**  
Molecular structure of the monoclinic polymorph of 3,4-bis(6-bromopyridin-3-yl)-1,2,5-thiadiazole with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-x + 2, y, -z + \frac{3}{2}$ ]



**Figure 3**  
Part of the packing diagram of the triclinic polymorph of the title compound, showing the formation of a  $\pi$ - $\pi$ -stacked column along the  $b$  axis. For clarity H atoms have been omitted.

Merlino (1976), Mühlebach *et al.* (1986), Tomura & Yamashita (2010) and Suturina *et al.* (2011). One difference in the molecular structure between the two polymorphs is the orientation of the pyridyl substituents (Fig. 2).

In the crystal of the triclinic polymorph, molecules are linked by a weak non-bonding  $\text{Br} \cdots \text{N}$  interaction [ $\text{Br1} \cdots \text{N4} = 3.056(3) \text{ \AA}$ ]. Furthermore, a column of molecules is established along the  $b$  axis by  $\pi$ - $\pi$  stacking interactions between the pyridine N3/C3–C7 rings (Fig. 3). This column shows an alternating pattern of short and long contacts, with centroid–centroid distances of 3.5934 (15) and 3.7014 (16)  $\text{\AA}$ , respectively, and with ring slippages [distance between  $\text{Cg}(I)$  and perpendicular projection of  $\text{Cg}(J)$  on ring  $I$ ] of 1.344 and 1.822  $\text{\AA}$ . Additionally, two  $\text{Br1} \cdots \pi$ -aryl contacts towards the thiazazole ring are found [ $\text{Br1} \cdots \text{Cg}(\text{S1/N1/C1/C2/N2})$  3.6815 (11) and 3.7659 (12)  $\text{\AA}$ ]. The other bromine atom shows a short intermolecular  $\text{Br} \cdots \text{Br}$  contact [ $\text{Br2} \cdots \text{Br2}$  3.3791 (6)  $\text{\AA}$ ] and a  $\text{Br} \cdots \pi$ -aryl contact towards the N4/C8–C12 pyridine ring [ $\text{Br2} \cdots \text{Cg}(\text{N4/C8–C12})$  3.6577 (11)  $\text{\AA}$ ]. In the monoclinic polymorph, the molecules are linked by intermolecular non-bonding  $\text{Br} \cdots \text{N}$  interactions (3.190  $\text{\AA}$ ), and  $\text{Br} \cdots \pi$ -aryl contacts can be observed as well [ $\text{Br} \cdots \text{Cg}(\text{thiadiazole})$  3.6748 (13)  $\text{\AA}$ ], but no intermolecular  $\text{Br} \cdots \text{Br}$  contacts or  $\pi$ - $\pi$  stacking interactions are present.

### Synthesis and crystallization

$[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{N}=\text{C}(\text{R})-\text{C}(\text{R})=\text{N})]$  ( $\text{R} = 6\text{-Br-3-py}$ ) (0.034 g, 0.05 mmol) were dissolved in  $\text{C}_6\text{D}_6$  and the red solution was transferred into a sealable J-Young NMR tube. A 0.2 M toluene solution of  $\text{SOCl}_2$  (0.25 ml, 0.05 mmol) was then

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	C <sub>12</sub> H <sub>6</sub> Br <sub>2</sub> N <sub>4</sub> S
$M_r$	398.09
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
$a, b, c$ (Å)	7.1617 (4), 7.2787 (4), 14.4257 (8)
$\alpha, \beta, \gamma$ (°)	77.0382 (9), 78.7453 (8), 61.5479 (7)
$V$ (Å <sup>3</sup> )	640.88 (6)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	6.48
Crystal size (mm)	0.49 × 0.36 × 0.19
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2014)
$T_{\min}, T_{\max}$	0.24, 0.38
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	8969, 2957, 2672
$R_{\text{int}}$	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.075, 1.06
No. of reflections	2957
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.52, -0.84

Computer programs: APEX2 (Bruker, 2014), SAINT (Bruker, 2013), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), XP in SHELXTL (Sheldrick, 2008), Mercury (Macrae *et al.*, 2006), publCIF (Westrip, 2010) and PLATON (Spek, 2009).

added *via* syringe and the mixture was warmed to 60°C for 7 d. Upon cooling to ambient temperature, yellow crystals formed (Becker *et al.*, 2016).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were placed in idealized positions with  $d(\text{C}-\text{H}) = 0.95$  Å and refined using a riding model with  $U_{\text{iso}}(\text{H})$  fixed at  $1.2U_{\text{eq}}(\text{C})$ .

## Acknowledgements

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## full crystallographic data

*IUCrData* (2016). **1**, x160960 [doi:10.1107/S2414314616009603]

## A second polymorph of 3,4-bis(6-bromopyridin-3-yl)-1,2,5-thiadiazole

Lisanne Becker, Kai Altenburger, Anke Spannenberg, Perdita Arndt and Uwe Rosenthal

## 3,4-Bis(6-bromopyridin-3-yl)-1,2,5-thiadiazole

*Crystal data*

$C_{12}H_6Br_2N_4S$

$M_r = 398.09$

Triclinic,  $P\bar{1}$

$a = 7.1617$  (4) Å

$b = 7.2787$  (4) Å

$c = 14.4257$  (8) Å

$\alpha = 77.0382$  (9)°

$\beta = 78.7453$  (8)°

$\gamma = 61.5479$  (7)°

$V = 640.88$  (6) Å<sup>3</sup>

$Z = 2$

$F(000) = 384$

$D_x = 2.063$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5554 reflections

$\theta = 2.9$ – $28.7$ °

$\mu = 6.48$  mm<sup>-1</sup>

$T = 150$  K

Prism, yellow

$0.49 \times 0.36 \times 0.19$  mm

*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.24$ ,  $T_{\max} = 0.38$

8969 measured reflections

2957 independent reflections

2672 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 1.5$ °

$h = -8 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 18$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.075$

$S = 1.06$

2957 reflections

172 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 1.1147P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.52$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.84$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.76469 (5)	0.11355 (4)	1.18285 (2)	0.02297 (9)
Br2	1.23819 (5)	0.06797 (5)	0.53206 (2)	0.02999 (10)
C1	0.2757 (4)	0.3696 (4)	0.83700 (18)	0.0127 (5)
C2	0.3420 (4)	0.3729 (4)	0.73593 (18)	0.0138 (5)
C3	0.4074 (4)	0.3033 (4)	0.91690 (17)	0.0122 (5)
C4	0.3258 (4)	0.2520 (4)	1.00972 (18)	0.0145 (5)
H4	0.1887	0.2566	1.0185	0.017*
C5	0.6206 (4)	0.1910 (4)	1.07289 (18)	0.0148 (5)
C6	0.7177 (4)	0.2399 (4)	0.98464 (19)	0.0172 (5)
H6	0.8552	0.2333	0.9785	0.021*
C7	0.6078 (4)	0.2985 (4)	0.90591 (18)	0.0157 (5)
H7	0.6683	0.3356	0.8444	0.019*
C8	0.5597 (4)	0.3033 (4)	0.68630 (17)	0.0141 (5)
C9	0.7254 (4)	0.1039 (4)	0.71185 (18)	0.0175 (5)
H9	0.6961	0.0110	0.7634	0.021*
C10	0.9576 (4)	0.1674 (4)	0.59460 (18)	0.0160 (5)
C11	0.8063 (4)	0.3673 (4)	0.56073 (19)	0.0188 (5)
H11	0.8404	0.4529	0.5070	0.023*
C12	0.6036 (4)	0.4365 (4)	0.60855 (18)	0.0166 (5)
H12	0.4946	0.5736	0.5889	0.020*
N1	0.0649 (4)	0.4469 (3)	0.85706 (16)	0.0164 (4)
N2	0.1799 (4)	0.4540 (4)	0.68361 (16)	0.0182 (4)
N3	0.4294 (4)	0.1969 (3)	1.08689 (15)	0.0156 (4)
N4	0.9244 (4)	0.0363 (3)	0.66717 (16)	0.0178 (4)
S1	-0.03875 (11)	0.52048 (11)	0.75638 (5)	0.01999 (15)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02748 (16)	0.02225 (14)	0.01974 (15)	-0.01104 (12)	-0.00918 (11)	0.00111 (10)
Br2	0.02001 (16)	0.03454 (17)	0.03315 (18)	-0.01163 (13)	0.00630 (12)	-0.01040 (13)
C1	0.0121 (11)	0.0133 (10)	0.0126 (11)	-0.0065 (9)	0.0006 (9)	-0.0014 (9)
C2	0.0148 (12)	0.0137 (11)	0.0121 (11)	-0.0070 (9)	0.0000 (9)	-0.0001 (9)
C3	0.0133 (12)	0.0116 (10)	0.0110 (11)	-0.0058 (9)	0.0010 (9)	-0.0020 (8)
C4	0.0135 (12)	0.0160 (11)	0.0135 (12)	-0.0071 (9)	0.0015 (10)	-0.0029 (9)
C5	0.0186 (13)	0.0126 (10)	0.0129 (11)	-0.0065 (10)	-0.0028 (10)	-0.0016 (9)
C6	0.0149 (12)	0.0194 (12)	0.0187 (13)	-0.0097 (10)	0.0007 (10)	-0.0032 (10)
C7	0.0159 (12)	0.0195 (12)	0.0128 (12)	-0.0105 (10)	0.0023 (10)	-0.0022 (9)
C8	0.0144 (12)	0.0172 (11)	0.0096 (11)	-0.0069 (10)	0.0001 (9)	-0.0019 (9)
C9	0.0181 (13)	0.0173 (12)	0.0123 (12)	-0.0067 (10)	0.0007 (10)	0.0013 (9)
C10	0.0124 (12)	0.0228 (12)	0.0137 (12)	-0.0083 (10)	0.0020 (10)	-0.0064 (10)
C11	0.0197 (13)	0.0226 (12)	0.0129 (12)	-0.0116 (11)	-0.0003 (10)	0.0028 (10)
C12	0.0142 (12)	0.0170 (11)	0.0135 (12)	-0.0051 (10)	-0.0013 (10)	0.0024 (9)
N1	0.0145 (11)	0.0187 (10)	0.0145 (10)	-0.0073 (9)	-0.0004 (9)	-0.0016 (8)
N2	0.0157 (11)	0.0233 (11)	0.0127 (10)	-0.0080 (9)	0.0002 (9)	-0.0004 (8)

N3	0.0179 (11)	0.0162 (10)	0.0124 (10)	-0.0086 (9)	-0.0001 (8)	-0.0009 (8)
N4	0.0145 (11)	0.0194 (10)	0.0152 (10)	-0.0046 (9)	-0.0008 (9)	-0.0024 (8)
S1	0.0127 (3)	0.0278 (3)	0.0158 (3)	-0.0076 (3)	-0.0012 (2)	-0.0004 (2)

*Geometric parameters (Å, °)*

Br1—C5	1.893 (3)	C6—H6	0.9500
Br2—C10	1.891 (3)	C7—H7	0.9500
C1—N1	1.332 (3)	C8—C9	1.393 (3)
C1—C2	1.441 (3)	C8—C12	1.401 (3)
C1—C3	1.480 (3)	C9—N4	1.344 (3)
C2—N2	1.324 (3)	C9—H9	0.9500
C2—C8	1.475 (4)	C10—N4	1.317 (3)
C3—C4	1.397 (3)	C10—C11	1.384 (4)
C3—C7	1.397 (4)	C11—C12	1.380 (4)
C4—N3	1.338 (3)	C11—H11	0.9500
C4—H4	0.9500	C12—H12	0.9500
C5—N3	1.326 (3)	N1—S1	1.625 (2)
C5—C6	1.385 (4)	N2—S1	1.629 (2)
C6—C7	1.379 (4)		
N1—C1—C2	112.7 (2)	C9—C8—C12	117.8 (2)
N1—C1—C3	118.3 (2)	C9—C8—C2	122.2 (2)
C2—C1—C3	128.9 (2)	C12—C8—C2	120.0 (2)
N2—C2—C1	113.1 (2)	N4—C9—C8	123.3 (2)
N2—C2—C8	118.3 (2)	N4—C9—H9	118.4
C1—C2—C8	128.6 (2)	C8—C9—H9	118.4
C4—C3—C7	117.0 (2)	N4—C10—C11	125.8 (2)
C4—C3—C1	119.3 (2)	N4—C10—Br2	115.89 (19)
C7—C3—C1	123.6 (2)	C11—C10—Br2	118.3 (2)
N3—C4—C3	123.8 (2)	C12—C11—C10	116.9 (2)
N3—C4—H4	118.1	C12—C11—H11	121.5
C3—C4—H4	118.1	C10—C11—H11	121.5
N3—C5—C6	124.5 (2)	C11—C12—C8	119.5 (2)
N3—C5—Br1	116.56 (19)	C11—C12—H12	120.2
C6—C5—Br1	118.9 (2)	C8—C12—H12	120.2
C7—C6—C5	117.7 (2)	C1—N1—S1	107.62 (18)
C7—C6—H6	121.2	C2—N2—S1	107.62 (18)
C5—C6—H6	121.2	C5—N3—C4	117.1 (2)
C6—C7—C3	119.9 (2)	C10—N4—C9	116.6 (2)
C6—C7—H7	120.1	N1—S1—N2	98.99 (12)
C3—C7—H7	120.1		
N1—C1—C2—N2	0.7 (3)	C12—C8—C9—N4	1.6 (4)
C3—C1—C2—N2	-176.1 (2)	C2—C8—C9—N4	179.4 (2)
N1—C1—C2—C8	179.3 (2)	N4—C10—C11—C12	1.3 (4)
C3—C1—C2—C8	2.5 (4)	Br2—C10—C11—C12	-179.2 (2)
N1—C1—C3—C4	22.4 (3)	C10—C11—C12—C8	-1.1 (4)

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C2—C1—C3—C4	-160.9 (2)	C9—C8—C12—C11	-0.2 (4)
N1—C1—C3—C7	-154.3 (2)	C2—C8—C12—C11	-178.0 (2)
C2—C1—C3—C7	22.4 (4)	C2—C1—N1—S1	-0.9 (2)
C7—C3—C4—N3	-0.9 (4)	C3—C1—N1—S1	176.28 (17)
C1—C3—C4—N3	-177.8 (2)	C1—C2—N2—S1	-0.1 (3)
N3—C5—C6—C7	-0.1 (4)	C8—C2—N2—S1	-178.87 (18)
Br1—C5—C6—C7	-179.15 (19)	C6—C5—N3—C4	0.7 (4)
C5—C6—C7—C3	-1.1 (4)	Br1—C5—N3—C4	179.80 (17)
C4—C3—C7—C6	1.5 (4)	C3—C4—N3—C5	-0.2 (4)
C1—C3—C7—C6	178.3 (2)	C11—C10—N4—C9	0.1 (4)
N2—C2—C8—C9	-129.4 (3)	Br2—C10—N4—C9	-179.44 (19)
C1—C2—C8—C9	52.0 (4)	C8—C9—N4—C10	-1.6 (4)
N2—C2—C8—C12	48.3 (3)	C1—N1—S1—N2	0.78 (19)
C1—C2—C8—C12	-130.3 (3)	C2—N2—S1—N1	-0.4 (2)

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