IUCrData

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4-(4-Bromophenyl)-2-(3-(4-chlorophenyl)-5-{3-[5-methyl-1-(4-methylphenyl)-1*H*-1,2,3-triazol-4-yl]-1-phenyl-1*H*-pyrazol-4-yl}-4,5-dihydro-1*H*-pyrazol-1-yl)thiazole

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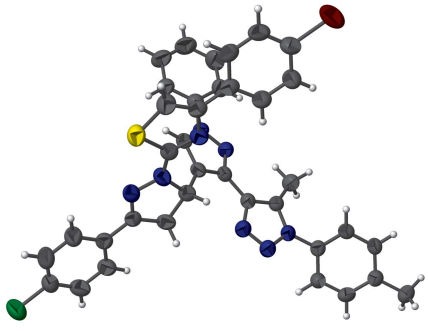
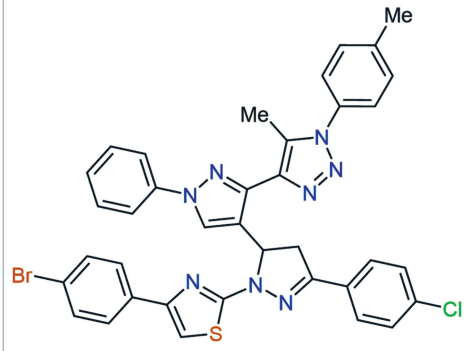
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{37}H_{28}BrClN_8O$, the linked chlorophenyl, pyrazolyl and thiazolyl ringss are almost coplanar, with dihedral angles of 0.6 (3)° between the chlorophenyl and pyrazolyl rings and 5.4 (3)° between the pyrazolyl and thiazolyl rings. The dihedral angle between the thiazolyl and bromophenyl rings is 17.5 (2)°. The central pyrazolyl rings subtend a dihedral angle of 67.7 (1)°. In the crystal, π–π and C—H···Br interactions link the molecules to form columns parallel to [010]. The π–π interactions involve partially overlapping nonparallel bromophenyl and tolyl groups.

3D view



Chemical scheme



Structure description

Various procedures have been reported for the synthesis of heterocycles containing the pyrazolinylthiazole moiety (Abdel-Wahab *et al.*, 2009; Abid & Azam, 2006; Bonacorso *et al.*, 2002). Both pyrazolyltriazoles and 1-thiazol-2-ylpyrazolines show various antimicrobial (Abdel-Wahab *et al.*, 2012, 2017), antitumor and antimycobacterial activities (Kumar *et al.*, 2003).

The asymmetric unit comprises a single molecule of $C_{37}H_{28}BrClN_8O$ (Fig. 1). Contact between neighbouring molecules includes π–π and C—H···Br interactions (Table 1, Fig. 2) to form columns parallel to [010]. The π–π interactions involve partially over-

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Br1^{i}	0.93	2.85	3.726 (4)	157

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

lapping bromophenyl and tolyl groups with a centroid-to-centroid distance of 3.993 (2) Å. The planes of the two groups are not parallel, however, with an interplanar angle of *ca* 15°.

Synthesis and crystallization

4-(4-Bromophenyl)-2-(3-(4-chlorophenyl)-5-{3-[5-methyl-1-(4-tolyl)-1*H*-1,2,3-triazol-4-yl]-1-phenyl-1*H*-pyrazol-4-yl}-4,5-dihydro-1*H*-pyrazol-1-yl)thiazole was synthesized in 83% yield from reaction of 3-(4-chlorophenyl)-5-{3-[5-methyl-1-(4-tolyl)-1*H*-1,2,3-triazol-4-yl]-1-phenyl-1*H*-pyrazol-4-yl}-4,5-dihydro-1*H*-pyrazole-1-carbothioamide and 2-bromo-1-(4-bromophenyl)ethanone in ethanol under reflux for 2 h.

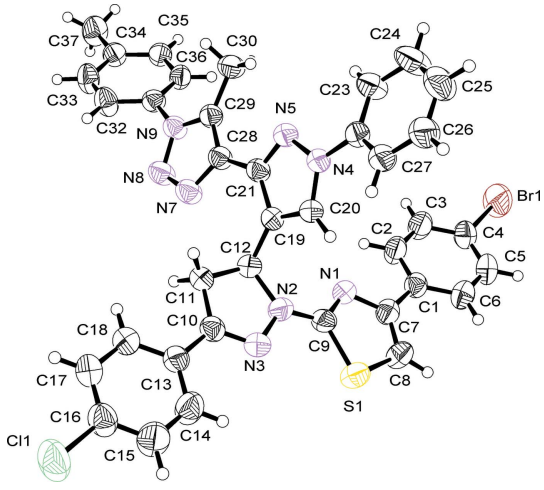


Figure 1
An *ORTEP* representation of the title molecule showing 50% probability ellipsoids.

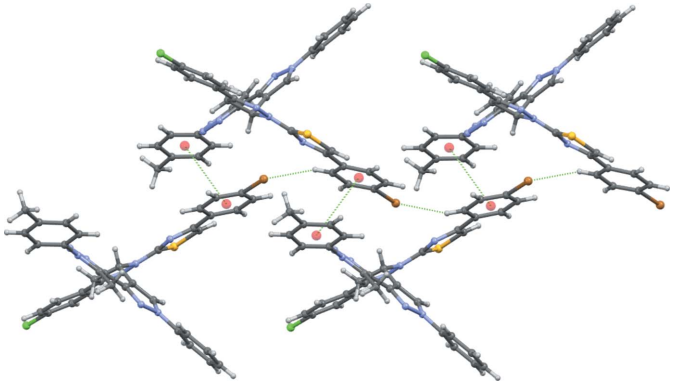


Figure 2
Part of the crystal structure showing intermolecular interactions as dotted lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{37}H_{28}BrClN_8S$
M_r	732.09
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	10.4220 (7), 13.4232 (5), 23.8943 (14)
β (°)	90.198 (6)
V (Å^3)	3342.7 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.41
Crystal size (mm)	0.42 × 0.10 × 0.04
Data collection	
Diffractometer	Agilent SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.794, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15250, 7792, 3958
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.702
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.183, 1.03
No. of reflections	7792
No. of parameters	435
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.95

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *CHEMDRAW Ultra* (Cambridge Soft, 2001).

Colourless crystals (m.p. 279–281°C, lit. 279–281°C; Abdel-Wahab *et al.*, 2017) were obtained by recrystallization of the crude product obtained following work-up using dimethylformamide as the solvent.

Refinement

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

Funding information

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full crystallographic data

IUCrData (2018). **3**, x180036 [https://doi.org/10.1107/S2414314618000366]

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Crystal data

$C_{37}H_{28}BrClN_8S$
M_r = 732.09
Monoclinic, $P2_1/n$
a = 10.4220 (7) Å
b = 13.4232 (5) Å
c = 23.8943 (14) Å
β = 90.198 (6)°
V = 3342.7 (3) Å^3
Z = 4
$F(000)$ = 1496
D_x = 1.455 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2941 reflections
θ = 3.5–23.9°
μ = 1.41 mm^{-1}
T = 296 K
Needle, colourless
0.42 × 0.10 × 0.04 mm

Data collection

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer
ω scans
Absorption correction: gaussian (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.794, T_{max} = 1.000
15250 measured reflections
7792 independent reflections
3958 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 29.9°, θ_{min} = 3.0°
h = −13→13
k = −18→13
l = −32→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.183
S = 1.03
7792 reflections
435 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 2.0474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.95 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.

Refinement. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Methine C—H bonds were fixed at 0.98 Å, with displacement parameters 1.2 times U_{eq}(C). Ethyl C—H bonds were fixed at 0.97 Å, with displacement parameters 1.2 times U_{eq}(C). Methyl C—H bonds were fixed at 0.96 Å, with displacement parameters 1.5 times U_{eq}(C), and were allowed to spin about the C—C bond. Aromatic C—H distances were set to 0.93 Å and their U_{iso}(H) set to 1.2 times the U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0099 (4)	0.4942 (3)	0.33097 (16)	0.0498 (9)
C2	−0.0953 (4)	0.5332 (3)	0.29246 (18)	0.0607 (11)
H2	−0.0901	0.6003	0.2831	0.073*
C3	−0.1882 (4)	0.4747 (3)	0.26767 (19)	0.0688 (12)
H3	−0.2451	0.5022	0.2419	0.083*
C4	−0.1960 (4)	0.3762 (3)	0.28134 (19)	0.0623 (11)
C5	−0.1140 (4)	0.3358 (3)	0.3204 (2)	0.0648 (12)
H5	−0.1209	0.2689	0.3300	0.078*
C6	−0.0220 (4)	0.3943 (3)	0.34518 (18)	0.0581 (11)
H6	0.0328	0.3668	0.3718	0.070*
C7	0.0919 (4)	0.5579 (3)	0.35531 (16)	0.0491 (9)
C8	0.1620 (4)	0.5379 (3)	0.40160 (18)	0.0597 (11)
H8	0.1527	0.4810	0.4234	0.072*
C9	0.2136 (4)	0.6910 (3)	0.35524 (15)	0.0482 (9)
C10	0.3825 (4)	0.9098 (3)	0.34920 (16)	0.0474 (9)
C11	0.3075 (4)	0.9318 (3)	0.29734 (16)	0.0568 (11)
H11A	0.3638	0.9422	0.2657	0.068*
H11B	0.2542	0.9903	0.3022	0.068*
C12	0.2252 (4)	0.8382 (3)	0.28926 (15)	0.0487 (9)
H12	0.1340	0.8544	0.2931	0.058*
C13	0.4759 (4)	0.9774 (3)	0.37459 (16)	0.0501 (9)
C14	0.5408 (4)	0.9515 (3)	0.4233 (2)	0.0715 (13)
H14	0.5252	0.8899	0.4399	0.086*
C15	0.6282 (5)	1.0159 (3)	0.4476 (2)	0.0831 (15)
H15	0.6713	0.9978	0.4802	0.100*
C16	0.6511 (4)	1.1068 (3)	0.4232 (2)	0.0659 (12)
C17	0.5883 (5)	1.1349 (3)	0.37556 (19)	0.0679 (12)
H17	0.6047	1.1966	0.3593	0.082*
C18	0.4996 (4)	1.0703 (3)	0.35153 (18)	0.0611 (11)
H18	0.4555	1.0898	0.3195	0.073*
C19	0.2493 (4)	0.7877 (2)	0.23490 (15)	0.0440 (8)
C20	0.3277 (4)	0.7084 (2)	0.22460 (15)	0.0471 (9)
H20	0.3740	0.6728	0.2513	0.057*
C21	0.2008 (4)	0.8139 (2)	0.18121 (15)	0.0449 (9)

C22	0.3920 (4)	0.6132 (2)	0.13991 (15)	0.0469 (9)
C23	0.3448 (4)	0.5813 (3)	0.08881 (17)	0.0611 (11)
H23	0.2739	0.6121	0.0726	0.073*
C24	0.4049 (5)	0.5027 (4)	0.0624 (2)	0.0838 (15)
H24	0.3743	0.4800	0.0281	0.101*
C25	0.5106 (5)	0.4577 (4)	0.0869 (2)	0.0829 (15)
H25	0.5501	0.4043	0.0691	0.099*
C26	0.5570 (5)	0.4910 (3)	0.1368 (2)	0.0729 (13)
H26	0.6286	0.4609	0.1528	0.087*
C27	0.4981 (4)	0.5691 (3)	0.16364 (17)	0.0568 (10)
H27	0.5299	0.5919	0.1977	0.068*
C28	0.1107 (4)	0.8942 (3)	0.16787 (15)	0.0456 (9)
C29	0.0411 (4)	0.9133 (3)	0.12035 (15)	0.0457 (9)
C30	0.0442 (4)	0.8669 (3)	0.06355 (16)	0.0575 (10)
H30A	−0.0321	0.8280	0.0579	0.086*
H30B	0.1182	0.8247	0.0606	0.086*
H30C	0.0483	0.9183	0.0357	0.086*
C31	−0.1280 (4)	1.0448 (3)	0.10234 (15)	0.0468 (9)
C32	−0.1308 (4)	1.1480 (3)	0.10141 (19)	0.0610 (11)
H32	−0.0677	1.1848	0.1197	0.073*
C33	−0.2283 (4)	1.1950 (3)	0.0731 (2)	0.0637 (12)
H33	−0.2305	1.2642	0.0729	0.076*
C34	−0.3234 (4)	1.1431 (3)	0.04488 (16)	0.0522 (9)
C35	−0.3173 (4)	1.0401 (3)	0.04686 (16)	0.0509 (9)
H35	−0.3799	1.0029	0.0285	0.061*
C36	−0.2212 (4)	0.9914 (3)	0.07533 (16)	0.0496 (9)
H36	−0.2195	0.9222	0.0762	0.060*
C37	−0.4290 (4)	1.1953 (3)	0.0139 (2)	0.0728 (13)
H37A	−0.4940	1.2158	0.0398	0.109*
H37B	−0.4657	1.1509	−0.0133	0.109*
H37C	−0.3949	1.2528	−0.0048	0.109*
N1	0.1209 (3)	0.6470 (2)	0.32887 (13)	0.0504 (8)
N2	0.2693 (3)	0.7769 (2)	0.33713 (13)	0.0543 (8)
N3	0.3588 (3)	0.8233 (2)	0.37024 (13)	0.0518 (8)
N4	0.3263 (3)	0.6905 (2)	0.16892 (12)	0.0453 (7)
N5	0.2478 (3)	0.7548 (2)	0.14118 (12)	0.0476 (7)
N7	0.0817 (3)	0.9641 (2)	0.20710 (13)	0.0566 (8)
N8	−0.0038 (3)	1.0250 (2)	0.18692 (14)	0.0565 (8)
N9	−0.0303 (3)	0.9945 (2)	0.13380 (13)	0.0475 (7)
Cl1	0.76129 (15)	1.18779 (9)	0.45379 (7)	0.1031 (5)
S1	0.27060 (11)	0.63119 (8)	0.41492 (5)	0.0611 (3)
Br1	−0.31987 (7)	0.29441 (4)	0.24515 (3)	0.1046 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.053 (2)	0.0446 (19)	0.052 (2)	0.0050 (17)	0.0076 (19)	0.0015 (17)
C2	0.068 (3)	0.044 (2)	0.070 (3)	−0.0030 (19)	−0.008 (2)	0.011 (2)

C3	0.077 (3)	0.053 (2)	0.075 (3)	−0.008 (2)	−0.022 (3)	0.011 (2)
C4	0.069 (3)	0.046 (2)	0.072 (3)	−0.0075 (19)	0.000 (2)	0.000 (2)
C5	0.070 (3)	0.0405 (19)	0.084 (3)	0.000 (2)	0.003 (3)	0.003 (2)
C6	0.056 (3)	0.050 (2)	0.069 (3)	0.0066 (19)	0.005 (2)	0.010 (2)
C7	0.049 (2)	0.0468 (19)	0.051 (2)	0.0057 (17)	0.0093 (19)	0.0021 (17)
C8	0.061 (3)	0.061 (2)	0.058 (3)	−0.004 (2)	−0.001 (2)	0.016 (2)
C9	0.053 (3)	0.051 (2)	0.041 (2)	0.0031 (18)	0.0031 (19)	−0.0026 (17)
C10	0.048 (2)	0.0457 (19)	0.048 (2)	0.0051 (17)	0.0010 (18)	−0.0052 (17)
C11	0.082 (3)	0.0433 (19)	0.045 (2)	0.0012 (19)	−0.008 (2)	−0.0041 (17)
C12	0.058 (2)	0.0469 (19)	0.041 (2)	0.0005 (17)	−0.0014 (18)	−0.0009 (16)
C13	0.053 (2)	0.048 (2)	0.049 (2)	0.0027 (17)	0.0001 (19)	−0.0025 (17)
C14	0.072 (3)	0.060 (2)	0.083 (3)	−0.008 (2)	−0.023 (3)	0.014 (2)
C15	0.078 (4)	0.075 (3)	0.096 (4)	−0.007 (3)	−0.038 (3)	0.011 (3)
C16	0.058 (3)	0.059 (2)	0.081 (3)	−0.005 (2)	−0.013 (2)	−0.005 (2)
C17	0.083 (3)	0.049 (2)	0.071 (3)	−0.006 (2)	−0.002 (3)	−0.002 (2)
C18	0.076 (3)	0.051 (2)	0.056 (2)	−0.001 (2)	−0.008 (2)	−0.0019 (19)
C19	0.050 (2)	0.0399 (17)	0.042 (2)	−0.0033 (16)	−0.0040 (17)	−0.0016 (15)
C20	0.059 (3)	0.0429 (19)	0.039 (2)	−0.0002 (17)	−0.0070 (18)	−0.0001 (15)
C21	0.046 (2)	0.0449 (18)	0.044 (2)	−0.0017 (16)	−0.0061 (17)	−0.0042 (16)
C22	0.052 (2)	0.0425 (18)	0.046 (2)	0.0005 (17)	0.0034 (18)	−0.0008 (16)
C23	0.061 (3)	0.070 (3)	0.052 (2)	0.004 (2)	−0.006 (2)	−0.014 (2)
C24	0.092 (4)	0.097 (3)	0.063 (3)	0.013 (3)	−0.014 (3)	−0.035 (3)
C25	0.096 (4)	0.074 (3)	0.079 (4)	0.026 (3)	0.003 (3)	−0.021 (3)
C26	0.088 (4)	0.067 (3)	0.063 (3)	0.025 (2)	−0.002 (3)	−0.006 (2)
C27	0.066 (3)	0.054 (2)	0.050 (2)	0.008 (2)	−0.006 (2)	−0.0020 (19)
C28	0.046 (2)	0.0460 (18)	0.044 (2)	0.0007 (16)	−0.0041 (17)	−0.0040 (16)
C29	0.047 (2)	0.0441 (18)	0.046 (2)	0.0012 (16)	−0.0046 (18)	−0.0011 (16)
C30	0.067 (3)	0.062 (2)	0.044 (2)	0.009 (2)	−0.004 (2)	−0.0053 (19)
C31	0.048 (2)	0.0485 (19)	0.044 (2)	0.0026 (17)	−0.0044 (18)	−0.0001 (17)
C32	0.055 (3)	0.049 (2)	0.079 (3)	0.0033 (19)	−0.019 (2)	−0.009 (2)
C33	0.064 (3)	0.041 (2)	0.085 (3)	0.0061 (19)	−0.009 (2)	−0.002 (2)
C34	0.051 (2)	0.052 (2)	0.054 (2)	0.0030 (18)	−0.0045 (19)	0.0001 (18)
C35	0.051 (2)	0.051 (2)	0.051 (2)	−0.0030 (18)	−0.0098 (19)	0.0009 (18)
C36	0.053 (2)	0.0419 (18)	0.054 (2)	−0.0043 (17)	−0.0038 (19)	0.0031 (17)
C37	0.068 (3)	0.061 (3)	0.089 (3)	0.012 (2)	−0.022 (3)	0.003 (2)
N1	0.061 (2)	0.0459 (16)	0.0442 (18)	−0.0017 (15)	−0.0005 (16)	0.0034 (14)
N2	0.068 (2)	0.0512 (17)	0.0442 (18)	−0.0110 (16)	−0.0103 (17)	0.0055 (15)
N3	0.057 (2)	0.0542 (18)	0.0445 (18)	−0.0003 (15)	−0.0053 (16)	−0.0008 (15)
N4	0.053 (2)	0.0412 (15)	0.0418 (17)	0.0041 (13)	−0.0021 (15)	−0.0017 (13)
N5	0.054 (2)	0.0466 (16)	0.0424 (17)	0.0032 (14)	−0.0062 (15)	−0.0001 (14)
N7	0.061 (2)	0.0561 (18)	0.053 (2)	0.0097 (16)	−0.0135 (17)	−0.0093 (16)
N8	0.060 (2)	0.0588 (19)	0.051 (2)	0.0098 (16)	−0.0119 (16)	−0.0110 (16)
N9	0.0463 (19)	0.0486 (16)	0.0476 (18)	0.0028 (14)	−0.0072 (15)	−0.0050 (14)
Cl1	0.1052 (12)	0.0701 (7)	0.1337 (13)	−0.0203 (7)	−0.0471 (10)	−0.0058 (8)
S1	0.0605 (7)	0.0698 (6)	0.0529 (6)	−0.0044 (5)	−0.0073 (5)	0.0115 (5)
Br1	0.1295 (6)	0.0716 (3)	0.1125 (5)	−0.0373 (3)	−0.0330 (4)	0.0029 (3)

Geometric parameters (Å, º)

C1—C2	1.381 (5)	C20—H20	0.9300
C1—C6	1.389 (5)	C21—N5	1.336 (4)
C1—C7	1.481 (5)	C21—C28	1.464 (5)
C2—C3	1.378 (6)	C22—C27	1.375 (5)
C2—H2	0.9300	C22—C23	1.383 (5)
C3—C4	1.365 (6)	C22—N4	1.424 (4)
C3—H3	0.9300	C23—C24	1.380 (6)
C4—C5	1.375 (6)	C23—H23	0.9300
C4—Br1	1.900 (4)	C24—C25	1.384 (6)
C5—C6	1.372 (6)	C24—H24	0.9300
C5—H5	0.9300	C25—C26	1.361 (6)
C6—H6	0.9300	C25—H25	0.9300
C7—C8	1.351 (5)	C26—C27	1.374 (6)
C7—N1	1.386 (5)	C26—H26	0.9300
C8—S1	1.717 (4)	C27—H27	0.9300
C8—H8	0.9300	C28—N7	1.361 (4)
C9—N1	1.295 (5)	C28—C29	1.370 (5)
C9—N2	1.362 (5)	C29—N9	1.360 (4)
C9—S1	1.739 (4)	C29—C30	1.493 (5)
C10—N3	1.289 (5)	C30—H30A	0.9600
C10—C13	1.461 (5)	C30—H30B	0.9600
C10—C11	1.493 (5)	C30—H30C	0.9600
C11—C12	1.532 (5)	C31—C36	1.367 (5)
C11—H11A	0.9700	C31—C32	1.385 (5)
C11—H11B	0.9700	C31—N9	1.433 (5)
C12—N2	1.481 (5)	C32—C33	1.372 (6)
C12—C19	1.487 (5)	C32—H32	0.9300
C12—H12	0.9800	C33—C34	1.385 (6)
C13—C18	1.387 (5)	C33—H33	0.9300
C13—C14	1.389 (6)	C34—C35	1.386 (5)
C14—C15	1.382 (6)	C34—C37	1.499 (5)
C14—H14	0.9300	C35—C36	1.374 (5)
C15—C16	1.373 (6)	C35—H35	0.9300
C15—H15	0.9300	C36—H36	0.9300
C16—C17	1.365 (6)	C37—H37A	0.9600
C16—Cl1	1.740 (4)	C37—H37B	0.9600
C17—C18	1.390 (6)	C37—H37C	0.9600
C17—H17	0.9300	N2—N3	1.371 (4)
C18—H18	0.9300	N4—N5	1.361 (4)
C19—C20	1.365 (5)	N7—N8	1.302 (4)
C19—C21	1.421 (5)	N8—N9	1.361 (4)
C20—N4	1.352 (4)		
C2—C1—C6	118.0 (4)	C27—C22—C23	120.9 (4)
C2—C1—C7	120.1 (3)	C27—C22—N4	120.0 (3)
C6—C1—C7	121.9 (4)	C23—C22—N4	119.0 (4)

C3—C2—C1	121.4 (4)	C24—C23—C22	118.7 (4)
C3—C2—H2	119.3	C24—C23—H23	120.7
C1—C2—H2	119.3	C22—C23—H23	120.7
C4—C3—C2	119.4 (4)	C23—C24—C25	120.1 (4)
C4—C3—H3	120.3	C23—C24—H24	119.9
C2—C3—H3	120.3	C25—C24—H24	119.9
C3—C4—C5	120.4 (4)	C26—C25—C24	120.4 (4)
C3—C4—Br1	119.5 (4)	C26—C25—H25	119.8
C5—C4—Br1	120.1 (3)	C24—C25—H25	119.8
C6—C5—C4	120.0 (4)	C25—C26—C27	120.1 (4)
C6—C5—H5	120.0	C25—C26—H26	119.9
C4—C5—H5	120.0	C27—C26—H26	119.9
C5—C6—C1	120.7 (4)	C26—C27—C22	119.7 (4)
C5—C6—H6	119.6	C26—C27—H27	120.1
C1—C6—H6	119.6	C22—C27—H27	120.1
C8—C7—N1	115.3 (4)	N7—C28—C29	108.9 (3)
C8—C7—C1	126.2 (3)	N7—C28—C21	120.1 (3)
N1—C7—C1	118.5 (3)	C29—C28—C21	131.0 (3)
C7—C8—S1	111.1 (3)	N9—C29—C28	104.0 (3)
C7—C8—H8	124.4	N9—C29—C30	124.2 (3)
S1—C8—H8	124.4	C28—C29—C30	131.5 (3)
N1—C9—N2	123.3 (3)	C29—C30—H30A	109.5
N1—C9—S1	116.1 (3)	C29—C30—H30B	109.5
N2—C9—S1	120.5 (3)	H30A—C30—H30B	109.5
N3—C10—C13	121.7 (3)	C29—C30—H30C	109.5
N3—C10—C11	113.7 (3)	H30A—C30—H30C	109.5
C13—C10—C11	124.6 (3)	H30B—C30—H30C	109.5
C10—C11—C12	103.5 (3)	C36—C31—C32	120.1 (4)
C10—C11—H11A	111.1	C36—C31—N9	120.2 (3)
C12—C11—H11A	111.1	C32—C31—N9	119.6 (3)
C10—C11—H11B	111.1	C33—C32—C31	118.9 (4)
C12—C11—H11B	111.1	C33—C32—H32	120.5
H11A—C11—H11B	109.0	C31—C32—H32	120.5
N2—C12—C19	111.6 (3)	C32—C33—C34	122.5 (4)
N2—C12—C11	100.7 (3)	C32—C33—H33	118.8
C19—C12—C11	112.8 (3)	C34—C33—H33	118.8
N2—C12—H12	110.4	C33—C34—C35	116.9 (4)
C19—C12—H12	110.4	C33—C34—C37	122.0 (4)
C11—C12—H12	110.4	C35—C34—C37	121.1 (4)
C18—C13—C14	118.1 (4)	C36—C35—C34	121.6 (4)
C18—C13—C10	120.9 (4)	C36—C35—H35	119.2
C14—C13—C10	120.9 (4)	C34—C35—H35	119.2
C15—C14—C13	120.9 (4)	C31—C36—C35	120.0 (3)
C15—C14—H14	119.6	C31—C36—H36	120.0
C13—C14—H14	119.6	C35—C36—H36	120.0
C16—C15—C14	119.6 (4)	C34—C37—H37A	109.5
C16—C15—H15	120.2	C34—C37—H37B	109.5
C14—C15—H15	120.2	H37A—C37—H37B	109.5

C17—C16—C15	121.1 (4)	C34—C37—H37C	109.5
C17—C16—Cl1	119.4 (3)	H37A—C37—H37C	109.5
C15—C16—Cl1	119.5 (4)	H37B—C37—H37C	109.5
C16—C17—C18	119.2 (4)	C9—N1—C7	109.6 (3)
C16—C17—H17	120.4	C9—N2—N3	119.4 (3)
C18—C17—H17	120.4	C9—N2—C12	125.8 (3)
C13—C18—C17	121.1 (4)	N3—N2—C12	113.7 (3)
C13—C18—H18	119.5	C10—N3—N2	108.3 (3)
C17—C18—H18	119.5	C20—N4—N5	111.8 (3)
C20—C19—C21	104.0 (3)	C20—N4—C22	127.2 (3)
C20—C19—C12	128.0 (3)	N5—N4—C22	121.0 (3)
C21—C19—C12	128.0 (3)	C21—N5—N4	104.4 (3)
N4—C20—C19	108.2 (3)	N8—N7—C28	109.4 (3)
N4—C20—H20	125.9	N7—N8—N9	107.0 (3)
C19—C20—H20	125.9	C29—N9—N8	110.7 (3)
N5—C21—C19	111.7 (3)	C29—N9—C31	130.0 (3)
N5—C21—C28	121.1 (3)	N8—N9—C31	119.3 (3)
C19—C21—C28	127.2 (3)	C8—S1—C9	87.82 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Br1^{i}	0.93	2.85	3.726 (4)	157

Symmetry code: (i) −*x*−1/2, *y*+1/2, −*z*+1/2.