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2-Phenylindolizine-3-carbaldehyde (4-phenylthiazol-2-yl)hydrazone hydrobromide monohydrate

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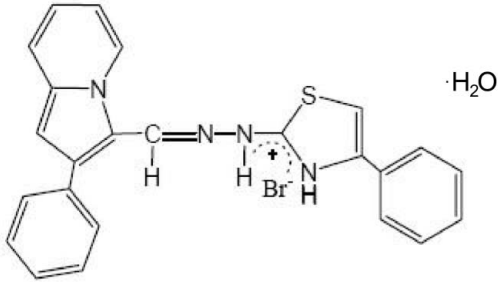
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.066; wR factor = 0.155; data-to-parameter ratio = 13.9.

In the title compound, $C_{24}H_{19}N_4S^+\cdot Br^-\cdot H_2O$, the thiazole and indolizine ring systems, together with the connecting NNC chain, form a nearly planar unit (r.m.s. deviation = 0.0786 Å). The component ions and water molecules are linked by N—H···O, N—H···Br and O—H···Br hydrogen bonds and weaker C—H···O, C—H···N and C—H···π interactions, forming chains along the *a* axis.

Related literature

For related literature, see: Eriksson *et al.* (2007); Gundersen *et al.* (2007); Sabb & Vogel (2007); Seethalakshmi *et al.* (2006); Smith *et al.* (2007).



Experimental

Crystal data

$C_{24}H_{19}N_4S^+\cdot Br^-\cdot H_2O$
M_r = 493.42
Monoclinic, $P2_1/n$
a = 6.1679 (12) Å
b = 11.1657 (18) Å
c = 32.640 (4) Å
β = 91.708 (2)°
V = 2246.9 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.95 mm^{-1}
T = 298 (2) K
0.42 × 0.36 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.495, T_{max} = 0.697
10856 measured reflections
3904 independent reflections
2795 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.155
S = 1.10
3904 reflections
280 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

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

Cg is the centroid of the pyridine ring (C14–C18/N4).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	1.90	2.744 (6)	166
O1—H1A···Br1	0.85	2.47	3.288 (5)	161
O1—H1B···Br1^{i}	0.85	2.52	3.337 (5)	161
N2—H2···Br1	0.86	2.62	3.359 (5)	144
C9—H9···O1	0.93	2.60	3.399 (7)	145
C18—H18···N3	0.93	2.42	2.984 (7)	119
C21—H21···Cg^{ii}	0.93	2.93	3.614	132

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2118).

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supplementary materials

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2-Phenylindolizine-3-carbaldehyde (4-phenylthiazol-2-yl)hydrazone hydrobromide monohydrate

W.-W. Liu, L. Wang, L.-J. Tang, W. Cao and H.-W. Hu

Comment

It is well known that both 1,3-thiazole and indolizine rings have a wide range of bioactivities. Some compounds with these rings have been used as sphingosine kinase inhibitors (Smith *et al.*, 2007), antitumor agents (Eriksson *et al.*, 2007), antituberculins (Gundersen *et al.*, 2007) and CNS agents (Sabb & Vogel, 2007). Hydrazones have also shown extensive bioactivities. The title compound was prepared to investigate additive properties of the groups.

The molecular structure of (I) is shown in Fig.1. The 1,3-thiazole ring has normal geometric parameters (Seethalakshmi *et al.*, 2006); the C1—S1[1.715 (5) Å] and C3—S1 [1.723 (6) Å] bond lengths are intermediate between typical C—S single- and double-bond distances, indicating significant electron delocalization. The C1—S1—C3 [89.3 (3)°] bond angle in (I) is almost the same as the corresponding value 89.81 (8)° in a related structure (Seethalakshmi *et al.*, 2006). The values of the C1—N2—N3—C10 [−178.4 (5)°] and N2—N3—C10—C11 [179.3 (5)°] torsion angles indicate that the C1—N2—N3—C10—C11 chain is nearly planar. The thiazole ring makes a dihedral angle of 9.5 (1)° with the N4/C11—C18 ring. Thus, a fully extended conjugated system is formed.

The molecular packing (Fig. 2) shows the occurrence of short intermolecular C—H···π interactions between C21—H21 and the pyridine ring (C14—C18/N4; centroid *Cg*), with a C21···*Cg* distance of 3.614 (6)Å (Table 1). Thus the two molecules form a centrosymmetric dimeric arrangement. As seen in Fig. 3, the water molecule acts as donor for intermolecular O—H···Br hydrogen bonds, and also acts as acceptor for an intermolecular N—H···O hydrogen bond. The Br^- anion acts as acceptor for an intermolecular N—H···Br hydrogen bond. Therefore, a chain is formed along the *a* axis *via* a combination of intermolecular N—H···O, N—H···Br and O—H···Br interactions.

Experimental

A solution of 3-formyl-2-phenylindozinethiosemicarbazone (0.12 g, 0.40 mmol) and ω-bromoacetophenone (0.085 g, 0.40 mmol) in anhydrous ethanol (10 ml) was stirred at room temperature, until all the thiosemicarbazone had disappeared (monitored by thin-layer chromatography). The resulting mixture was allowed to settle, and the title compound was collected by filtration and dried *in vacuo*. Dark green single crystals of (I) suitable for X-ray crystallographic analysis were obtained by recrystallization from 95% ethanol.

Refinement

All of the hydrogen atoms were placed in calculated positions, with C—H = 0.93, N—H = 0.86 and O—H = 0.85 Å, and with U_{iso}(H) = 1.5U_{eq}(parent).

Figures

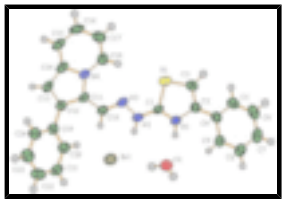

Fig. 1. A view of the asymmetric unit of (I), showing the atom-labelling scheme·Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.

Fig. 2. Part of the crystal structure of (I), viewed along the *a* axis. Showing the formation of a cyclic C—H···π (dashed lines) interaction.

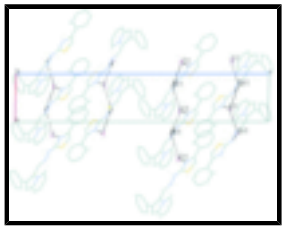

Fig. 3. A view down *a* axis of the unit-cell packing in (I), showing the linear molecular clusters. Hydrogen bonds are indicated by dashed lines.

2-Phenylindolizine-3-carbaldehyde (4-phenylthiazol-2-yl)hydrazone hydrobromide monohydrate

Crystal data

$C_{24}H_{19}N_4S^+·Br^-·H_2O$	F_{000} = 1008
M_r = 493.42	D_x = 1.459 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 6.1679 (12) Å	Cell parameters from 2831 reflections
b = 11.1657 (18) Å	θ = 2.2–22.5º
c = 32.640 (4) Å	μ = 1.95 mm^{-1}
β = 91.708 (2)º	T = 298 (2) K
V = 2246.9 (6) Å^3	Prism, dark green
Z = 4	0.42 × 0.36 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3904 independent reflections
Radiation source: fine-focus sealed tube	2795 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.058
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 1.9º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	h = −7→7
T_{min} = 0.495, T_{max} = 0.697	k = −13→13
10856 measured reflections	l = −28→38

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H-atom parameters constrained
$wR(F^2) = 0.155$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 4.8524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
3904 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.61$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.75959 (10)	0.38600 (5)	0.11839 (2)	0.0566 (2)
N1	0.3347 (7)	0.1191 (4)	0.18113 (13)	0.0385 (10)
H1	0.2916	0.1879	0.1723	0.046*
N2	0.6267 (7)	0.0997 (4)	0.13683 (13)	0.0412 (11)
H2	0.6065	0.1681	0.1252	0.049*
N3	0.7942 (7)	0.0233 (4)	0.12601 (14)	0.0402 (11)
N4	1.1713 (7)	−0.1100 (4)	0.09626 (13)	0.0404 (10)
O1	0.2693 (7)	0.3484 (4)	0.15315 (16)	0.0754 (14)
H1A	0.3790	0.3640	0.1389	0.091*
H1B	0.1548	0.3639	0.1390	0.091*
S1	0.5445 (3)	−0.07581 (13)	0.18834 (6)	0.0568 (5)
C1	0.5020 (8)	0.0612 (4)	0.16573 (16)	0.0349 (12)
C2	0.2345 (8)	0.0580 (5)	0.21305 (16)	0.0381 (12)
C3	0.3310 (10)	−0.0484 (6)	0.2199 (2)	0.0588 (17)
H3	0.2867	−0.1021	0.2397	0.071*
C4	0.0481 (9)	0.1089 (5)	0.23317 (16)	0.0410 (13)
C5	−0.0156 (10)	0.0657 (6)	0.27091 (18)	0.0538 (15)
H5	0.0686	0.0078	0.2843	0.065*

C6	−0.1995 (11)	0.1064 (6)	0.2888 (2)	0.0657 (19)
H6	−0.2419	0.0742	0.3136	0.079*
C7	−0.3215 (10)	0.1950 (6)	0.27000 (19)	0.0557 (16)
H7	−0.4467	0.2227	0.2821	0.067*
C8	−0.2584 (9)	0.2428 (5)	0.23340 (18)	0.0493 (14)
H8	−0.3393	0.3039	0.2211	0.059*
C9	−0.0750 (8)	0.2002 (5)	0.21481 (17)	0.0408 (13)
H9	−0.0335	0.2326	0.1900	0.049*
C10	0.9165 (8)	0.0641 (5)	0.09851 (16)	0.0379 (12)
H10	0.8847	0.1394	0.0878	0.046*
C11	1.0987 (8)	0.0020 (4)	0.08310 (16)	0.0368 (12)
C12	1.2477 (8)	0.0448 (5)	0.05520 (15)	0.0367 (12)
C13	1.4131 (9)	−0.0377 (5)	0.05280 (17)	0.0447 (14)
H13	1.5358	−0.0298	0.0371	0.054*
C14	1.3657 (9)	−0.1348 (5)	0.07770 (16)	0.0443 (14)
C15	1.4690 (10)	−0.2445 (6)	0.08584 (19)	0.0545 (16)
H15	1.6006	−0.2618	0.0740	0.065*
C16	1.3770 (12)	−0.3254 (6)	0.1111 (2)	0.0679 (19)
H16	1.4452	−0.3982	0.1166	0.081*
C17	1.1786 (12)	−0.2986 (6)	0.1288 (2)	0.0659 (19)
H17	1.1153	−0.3547	0.1458	0.079*
C18	1.0774 (10)	−0.1927 (5)	0.12170 (19)	0.0543 (16)
H18	0.9463	−0.1759	0.1338	0.065*
C19	1.2270 (9)	0.1601 (5)	0.03296 (15)	0.0376 (12)
C20	1.0416 (10)	0.1895 (5)	0.00987 (17)	0.0474 (14)
H20	0.9269	0.1355	0.0082	0.057*
C21	1.0248 (10)	0.2966 (6)	−0.01045 (19)	0.0555 (16)
H21	0.9003	0.3146	−0.0260	0.067*
C22	1.1929 (12)	0.3774 (6)	−0.0077 (2)	0.0663 (18)
H22	1.1811	0.4509	−0.0210	0.080*
C23	1.3781 (11)	0.3494 (6)	0.0146 (2)	0.071 (2)
H23	1.4925	0.4037	0.0161	0.085*
C24	1.3951 (10)	0.2421 (6)	0.0346 (2)	0.0576 (16)
H24	1.5217	0.2240	0.0495	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0546 (4)	0.0407 (3)	0.0742 (5)	0.0031 (3)	−0.0020 (3)	0.0023 (3)
N1	0.036 (2)	0.030 (2)	0.050 (3)	0.004 (2)	−0.002 (2)	0.002 (2)
N2	0.043 (3)	0.034 (2)	0.046 (3)	0.013 (2)	−0.001 (2)	0.003 (2)
N3	0.035 (3)	0.033 (2)	0.053 (3)	0.0100 (19)	−0.002 (2)	−0.004 (2)
N4	0.035 (2)	0.039 (2)	0.047 (3)	0.008 (2)	0.001 (2)	0.002 (2)
O1	0.052 (3)	0.059 (3)	0.116 (4)	0.006 (2)	0.007 (3)	0.034 (3)
S1	0.0525 (9)	0.0320 (8)	0.0862 (12)	0.0110 (6)	0.0066 (8)	0.0112 (7)
C1	0.027 (3)	0.032 (3)	0.045 (3)	0.004 (2)	−0.007 (2)	−0.001 (2)
C2	0.035 (3)	0.037 (3)	0.042 (3)	−0.007 (2)	−0.004 (2)	0.003 (2)
C3	0.053 (4)	0.050 (4)	0.074 (4)	0.005 (3)	0.010 (3)	0.022 (3)

C4	0.040 (3)	0.041 (3)	0.042 (3)	−0.009 (3)	−0.002 (2)	0.000 (3)
C5	0.060 (4)	0.052 (4)	0.050 (4)	0.000 (3)	0.001 (3)	0.014 (3)
C6	0.072 (5)	0.074 (5)	0.052 (4)	−0.009 (4)	0.022 (4)	0.001 (4)
C7	0.046 (4)	0.067 (4)	0.054 (4)	−0.006 (3)	0.011 (3)	−0.013 (3)
C8	0.043 (3)	0.050 (3)	0.055 (4)	0.004 (3)	0.003 (3)	−0.011 (3)
C9	0.039 (3)	0.043 (3)	0.041 (3)	−0.003 (2)	0.003 (2)	−0.003 (2)
C10	0.037 (3)	0.032 (3)	0.045 (3)	0.003 (2)	0.000 (3)	−0.004 (2)
C11	0.032 (3)	0.034 (3)	0.044 (3)	0.008 (2)	−0.004 (2)	−0.002 (2)
C12	0.038 (3)	0.039 (3)	0.033 (3)	0.001 (2)	−0.004 (2)	−0.003 (2)
C13	0.029 (3)	0.057 (4)	0.048 (3)	0.008 (3)	0.001 (2)	−0.005 (3)
C14	0.041 (3)	0.048 (3)	0.043 (3)	0.014 (3)	−0.003 (3)	−0.008 (3)
C15	0.046 (4)	0.059 (4)	0.058 (4)	0.026 (3)	−0.001 (3)	−0.010 (3)
C16	0.071 (5)	0.049 (4)	0.083 (5)	0.033 (3)	−0.002 (4)	0.009 (4)
C17	0.076 (5)	0.043 (4)	0.080 (5)	0.008 (3)	0.013 (4)	0.016 (3)
C18	0.049 (4)	0.047 (4)	0.068 (4)	0.006 (3)	0.013 (3)	0.006 (3)
C19	0.041 (3)	0.035 (3)	0.036 (3)	0.000 (2)	0.001 (2)	−0.008 (2)
C20	0.048 (4)	0.036 (3)	0.058 (4)	0.000 (3)	−0.002 (3)	−0.005 (3)
C21	0.046 (4)	0.055 (4)	0.065 (4)	0.014 (3)	−0.007 (3)	0.003 (3)
C22	0.079 (5)	0.039 (3)	0.082 (5)	0.008 (3)	0.003 (4)	0.008 (3)
C23	0.057 (4)	0.046 (4)	0.109 (6)	−0.018 (3)	−0.011 (4)	0.010 (4)
C24	0.050 (4)	0.056 (4)	0.066 (4)	−0.008 (3)	−0.008 (3)	0.011 (3)

Geometric parameters (Å, °)

N1—C1	1.329 (6)	C9—H9	0.930
N1—C2	1.404 (6)	C10—C11	1.424 (7)
N1—H1	0.860	C10—H10	0.930
N2—C1	1.308 (6)	C11—C12	1.397 (7)
N2—N3	1.394 (6)	C12—C13	1.379 (7)
N2—H2	0.860	C12—C19	1.481 (7)
N3—C10	1.274 (6)	C13—C14	1.391 (8)
N4—C18	1.381 (7)	C13—H13	0.930
N4—C14	1.388 (7)	C14—C15	1.403 (8)
N4—C11	1.392 (6)	C15—C16	1.358 (9)
O1—H1A	0.850	C15—H15	0.930
O1—H1B	0.850	C16—C17	1.401 (9)
S1—C1	1.715 (5)	C16—H16	0.930
S1—C3	1.723 (6)	C17—C18	1.354 (8)
C2—C3	1.344 (8)	C17—H17	0.930
C2—C4	1.456 (7)	C18—H18	0.930
C3—H3	0.930	C19—C24	1.384 (8)
C4—C5	1.391 (8)	C19—C20	1.390 (8)
C4—C9	1.396 (7)	C20—C21	1.369 (8)
C5—C6	1.369 (9)	C20—H20	0.930
C5—H5	0.930	C21—C22	1.375 (9)
C6—C7	1.377 (9)	C21—H21	0.930
C6—H6	0.930	C22—C23	1.372 (10)
C7—C8	1.375 (8)	C22—H22	0.930
C7—H7	0.930	C23—C24	1.367 (9)

C8—C9	1.384 (7)	C23—H23	0.930
C8—H8	0.930	C24—H24	0.930
C1—N1—C2	114.1 (4)	N4—C11—C12	107.3 (4)
C1—N1—H1	123.0	N4—C11—C10	125.3 (5)
C2—N1—H1	123.0	C12—C11—C10	127.2 (5)
C1—N2—N3	115.9 (4)	C13—C12—C11	108.1 (5)
C1—N2—H2	122.0	C13—C12—C19	127.3 (5)
N3—N2—H2	122.0	C11—C12—C19	124.6 (5)
C10—N3—N2	114.8 (4)	C12—C13—C14	108.6 (5)
C18—N4—C14	120.8 (5)	C12—C13—H13	125.7
C18—N4—C11	130.5 (4)	C14—C13—H13	125.7
C14—N4—C11	108.6 (4)	N4—C14—C13	107.4 (5)
H1A—O1—H1B	108.8	N4—C14—C15	119.0 (5)
C1—S1—C3	89.3 (3)	C13—C14—C15	133.6 (5)
N2—C1—N1	126.3 (5)	C16—C15—C14	120.0 (5)
N2—C1—S1	121.2 (4)	C16—C15—H15	120.0
N1—C1—S1	112.4 (4)	C14—C15—H15	120.0
C3—C2—N1	110.5 (5)	C15—C16—C17	119.6 (6)
C3—C2—C4	128.5 (5)	C15—C16—H16	120.2
N1—C2—C4	121.1 (5)	C17—C16—H16	120.2
C2—C3—S1	113.6 (4)	C18—C17—C16	121.3 (6)
C2—C3—H3	123.2	C18—C17—H17	119.3
S1—C3—H3	123.2	C16—C17—H17	119.3
C5—C4—C9	118.0 (5)	C17—C18—N4	119.2 (5)
C5—C4—C2	120.8 (5)	C17—C18—H18	120.4
C9—C4—C2	121.2 (5)	N4—C18—H18	120.4
C6—C5—C4	121.5 (6)	C24—C19—C20	117.9 (5)
C6—C5—H5	119.2	C24—C19—C12	120.2 (5)
C4—C5—H5	119.2	C20—C19—C12	122.0 (5)
C5—C6—C7	119.8 (6)	C21—C20—C19	121.2 (6)
C5—C6—H6	120.1	C21—C20—H20	119.4
C7—C6—H6	120.1	C19—C20—H20	119.4
C8—C7—C6	120.1 (6)	C20—C21—C22	119.7 (6)
C8—C7—H7	120.0	C20—C21—H21	120.2
C6—C7—H7	120.0	C22—C21—H21	120.2
C7—C8—C9	120.3 (6)	C23—C22—C21	119.9 (6)
C7—C8—H8	119.9	C23—C22—H22	120.0
C9—C8—H8	119.9	C21—C22—H22	120.0
C8—C9—C4	120.2 (5)	C24—C23—C22	120.3 (6)
C8—C9—H9	119.9	C24—C23—H23	119.9
C4—C9—H9	119.9	C22—C23—H23	119.9
N3—C10—C11	124.4 (5)	C23—C24—C19	121.0 (6)
N3—C10—H10	117.8	C23—C24—H24	119.5
C11—C10—H10	117.8	C19—C24—H24	119.5
C1—N2—N3—C10	−178.4 (5)	N4—C11—C12—C13	−2.5 (6)
N3—N2—C1—N1	179.3 (5)	C10—C11—C12—C13	172.3 (5)
N3—N2—C1—S1	−0.3 (6)	N4—C11—C12—C19	178.1 (5)
C2—N1—C1—N2	−177.8 (5)	C10—C11—C12—C19	−7.2 (8)

C2—N1—C1—S1	1.9 (5)	C11—C12—C13—C14	2.4 (6)
C3—S1—C1—N2	178.4 (5)	C19—C12—C13—C14	−178.2 (5)
C3—S1—C1—N1	−1.3 (4)	C18—N4—C14—C13	177.3 (5)
C1—N1—C2—C3	−1.5 (7)	C11—N4—C14—C13	−0.3 (6)
C1—N1—C2—C4	−179.7 (5)	C18—N4—C14—C15	−1.4 (8)
N1—C2—C3—S1	0.5 (7)	C11—N4—C14—C15	−179.0 (5)
C4—C2—C3—S1	178.5 (4)	C12—C13—C14—N4	−1.3 (6)
C1—S1—C3—C2	0.4 (5)	C12—C13—C14—C15	177.2 (6)
C3—C2—C4—C5	19.0 (9)	N4—C14—C15—C16	1.0 (9)
N1—C2—C4—C5	−163.1 (5)	C13—C14—C15—C16	−177.4 (7)
C3—C2—C4—C9	−159.4 (6)	C14—C15—C16—C17	0.1 (10)
N1—C2—C4—C9	18.4 (8)	C15—C16—C17—C18	−0.8 (11)
C9—C4—C5—C6	3.4 (9)	C16—C17—C18—N4	0.4 (11)
C2—C4—C5—C6	−175.1 (6)	C14—N4—C18—C17	0.7 (9)
C4—C5—C6—C7	−2.3 (10)	C11—N4—C18—C17	177.7 (6)
C5—C6—C7—C8	−0.2 (10)	C13—C12—C19—C24	−52.9 (8)
C6—C7—C8—C9	1.5 (9)	C11—C12—C19—C24	126.5 (6)
C7—C8—C9—C4	−0.3 (8)	C13—C12—C19—C20	126.8 (6)
C5—C4—C9—C8	−2.1 (8)	C11—C12—C19—C20	−53.8 (7)
C2—C4—C9—C8	176.4 (5)	C24—C19—C20—C21	−0.4 (8)
N2—N3—C10—C11	179.3 (5)	C12—C19—C20—C21	179.9 (5)
C18—N4—C11—C12	−175.6 (5)	C19—C20—C21—C22	−0.7 (9)
C14—N4—C11—C12	1.7 (6)	C20—C21—C22—C23	1.3 (10)
C18—N4—C11—C10	9.5 (9)	C21—C22—C23—C24	−0.9 (11)
C14—N4—C11—C10	−173.2 (5)	C22—C23—C24—C19	−0.3 (11)
N3—C10—C11—N4	−1.3 (8)	C20—C19—C24—C23	0.9 (9)
N3—C10—C11—C12	−175.1 (5)	C12—C19—C24—C23	−179.4 (6)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.90	2.744 (6)	166
O1—H1A···Br1	0.85	2.47	3.288 (5)	161
O1—H1B···Br1^{i}	0.85	2.52	3.337 (5)	161
N2—H2···Br1	0.86	2.62	3.359 (5)	144
C9—H9···O1	0.93	2.60	3.399 (7)	145
C18—H18···N3	0.93	2.42	2.984 (7)	119
C21—H21···Cg^{ii}	0.93	2.93	3.614	132

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

Fig. 1

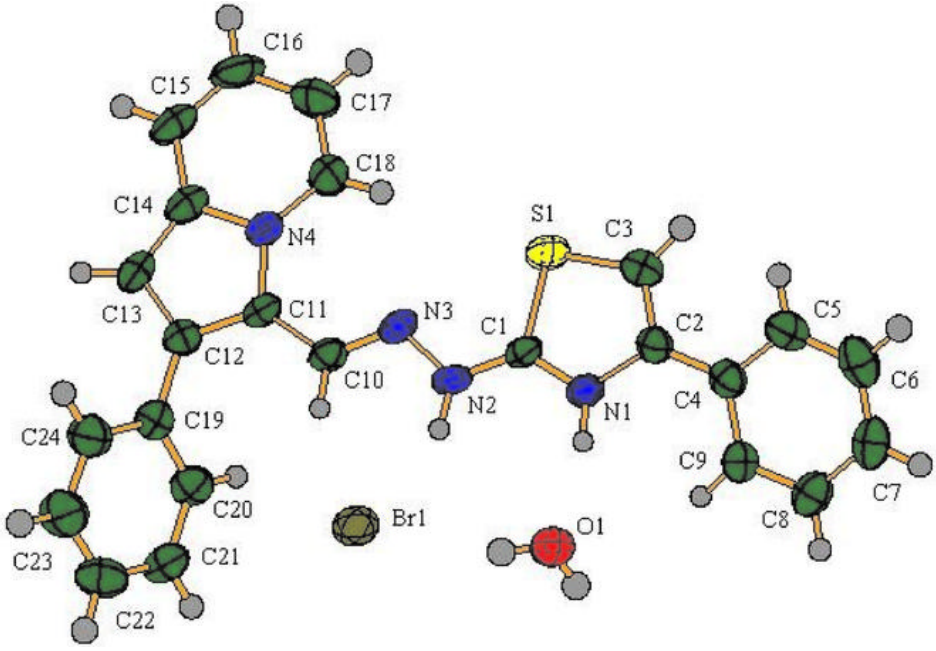
C16
C15
C17
C18
C14
N4
S1
C3
C13
C11
N3
C1
C2
C5
C12
C10
N2
N1
C4
C6
C24
C19
C9
C7
C20
Br1
O1
C8
C23
C21
C22

Fig. 2

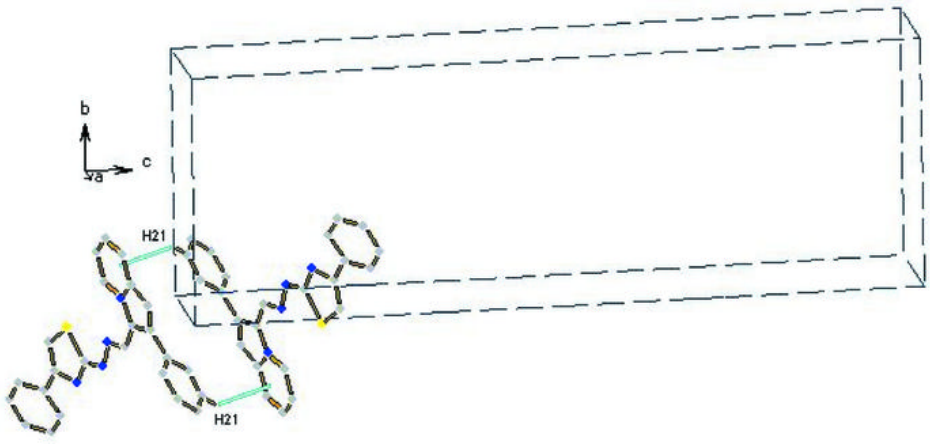

Fig. 3