



Synthesis and crystal structure of 3-(adamantan-1-yl)-4-(2-bromo-4-fluorophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Received 28 October 2019

Accepted 6 January 2020

Edited by C. Massera, Università di Parma, Italy

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Keywords: crystal structure; adamantane; triazole.

CCDC reference: 1975689

Supporting information: this article has supporting information at journals.iucr.org/e

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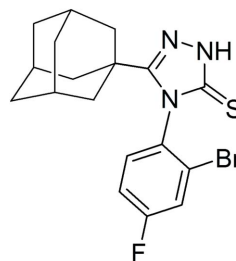
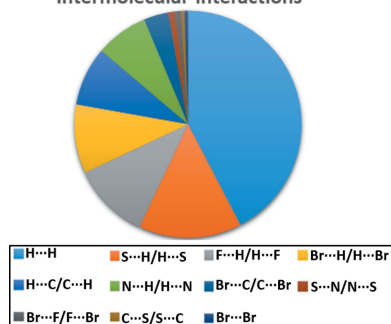
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In the title compound, C₁₈H₁₉BrFN₃S, the 1,2,4-triazole ring is nearly planar with a maximum deviation of −0.009 (3) and 0.009 (4) Å, respectively, for the S-bound C atom and the N atom bonded to the bromofluorophenyl ring. The phenyl and triazole rings are almost perpendicular to each other, forming a dihedral angle of 89.5 (2)°. In the crystal, the molecules are linked by weak C—H···π(phenyl) interactions, forming supramolecular chains extending along the *c*-axis direction. The crystal packing is further consolidated by intermolecular N—H···S hydrogen bonds and by weak C—H···S interactions, yielding double chains propagating along the *a*-axis direction. The crystal studied was refined as a racemic twin.

1. Chemical context

Adamantane derivatives are currently receiving considerable interest for their diverse biological activities (Liu *et al.*, 2011; Lamoureux & Artavia, 2010). Numerous adamantane-based drugs have been developed as antiviral (Davies *et al.*, 1964; Togo *et al.*, 1968; Rosenthal *et al.*, 1982; El-Emam *et al.*, 2004; Burstein *et al.*, 1999; Balzarini *et al.*, 2009), anticancer (Sun *et al.*, 2002; Min *et al.*, 2017), antidiabetic (Villhauer *et al.*, 2003 & Augeri *et al.*, 2005), anti-Parkinsonian (Schwab *et al.*, 1969), anti-Alzheimer's (Bormann, 1989) and antipsychotic (Abou-Gharbia *et al.*, 1999) agents. In addition, several adamantane-based analogues have been shown to possess promising bactericidal (Protopopova *et al.*, 2005; El-Emam *et al.*, 2013; Kadi *et al.*, 2010; Al-Abdullah *et al.*, 2014; Al-Deeb *et al.*, 2006) and fungicidal (Omar *et al.*, 2010) activities. On the other hand, 1,2,4-triazole derivatives have been reported to possess significant anti-inflammatory (Navidpour *et al.*, 2006) and antibacterial activities (Almajan *et al.*, 2009). Based on the diverse biological activities of adamantane and 1,2,4-triazole derivatives, we synthesized the title 1,2,4-triazole-adamantane hybrid derivative **I** as potential chemotherapeutic agent.

Intermolecular interactions



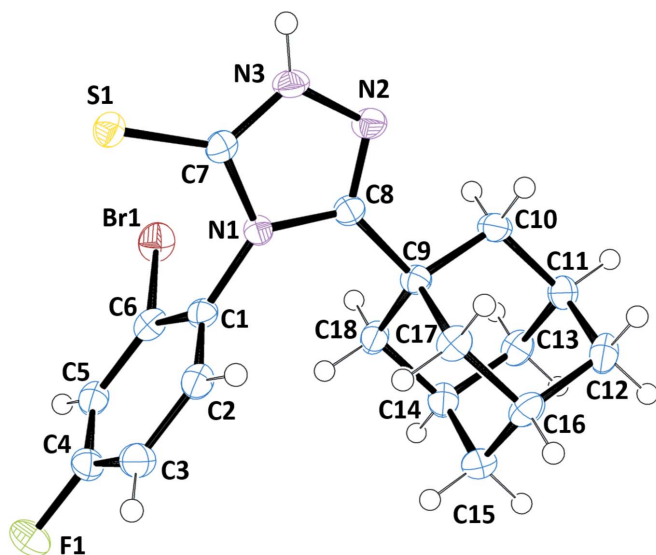


Figure 1
The molecular structure of the title compound with atom labels, showing displacement ellipsoids at the 50% probability level.

2. Structural commentary

In the title molecule (Fig. 1), the 1,2,4-triazole ring (N1–N3/C7/C8) is nearly planar with a maximum deviation of -0.009 (3) Å for atom C7 and 0.009 (4) Å for atom N1. The phenyl ring (C1–C6) is almost perpendicular to the 1,2,4-triazole ring, forming a dihedral angle of 89.5 (2)°. The triazole ring is substituted in positions 3 and 5 with an adamantane group and a sulfur atom which deviate from the mean plane of the ring of -0.149 (4) and -0.067 (1) Å, respectively. The phenyl group is substituted at positions 2 and 4 by a bromine and a fluorine atom, which deviate by 0.001 (4) and 0.014 (2) Å, respectively, from the ring plane. The bond distances are in normal ranges for this type of compound [C4–F1 = 1.355 (4), C6–Br1 = 1.898 (3) and C7–S1 = 1.688 (3) Å]. The double-bond character of the C8=N2 bond

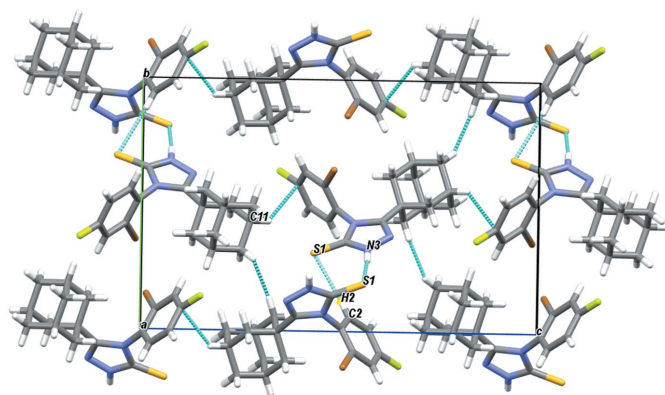


Figure 2
A view of the packing of **I** along the *a*-axis direction. The N–H···S hydrogen bonds and C–H···S and C–H··· π interactions are shown as dashed lines.

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

Cg2 is the centroid of the C1–C2 ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N3–H3N···S1 ⁱ	0.86	2.62	3.461 (3)	166
C2–H2···S1 ⁱⁱ	0.93	2.8	3.683 (3)	160
C11–H11···Cg2 ⁱⁱⁱ	0.98	2.86	3.757 (4)	152

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

is evidenced by its length of 1.288 (4) Å, while the other distances in the triazole ring are indicative of electronic delocalization [N2–N3, C7–N3 and C7–N1 = 1.377 (4), 1.327 (4) and 1.379 (4) Å, respectively].

3. Supramolecular features

In the crystal (Fig. 2), the molecules are linked by weak interaction of the type C–H··· π (phenyl), forming supramolecular chains extending along the *c*-axis direction, involving the C11–H11 group of the adamantane moiety and the C1–C6 aromatic ring. The crystal packing is further consolidated by intermolecular N3–H3N···S1($x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$) hydrogen bonds, in which the triazole ring behaves both as donor and acceptor, and by weak C2–H2···S1($x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$) interactions (Table 1), yielding double chains propagating along the *a*-axis direction.

4. Hirshfeld surface analysis

In order to investigate the intermolecular interactions in the structure of **I** in a visual manner, a Hirshfeld surface analysis was performed using the program *Crystal Explorer 17.5* (Spackman *et al.* 2002; Turner *et al.*, 2017). Fig. 3 shows the HS surfaces mapped over d_{norm} , shape-index and curvedness (Fig. 3). In the HS plotted over d_{norm} , white areas on the surface indicate contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distant contact) than the van der Waals radii, respectively. Two red spots are present in close proximity to the S and N–H atoms involved in hydrogen bonding. As expected, the absence of red and blue triangles on the shape-index surface and the small, flat segments delineated by the blue line in the surface mapped over curvedness indicate the absence of π – π stacking inter-

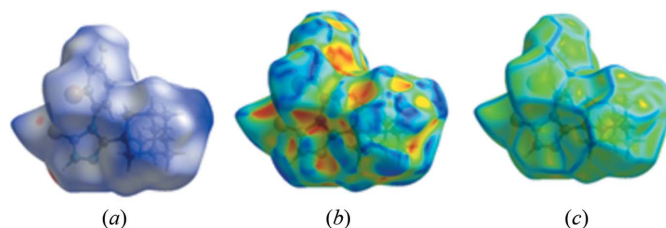


Figure 3
Hirshfeld surfaces of compound **I**, plotted over (a) d_{norm} , (b) shape-index and (c) curvedness.

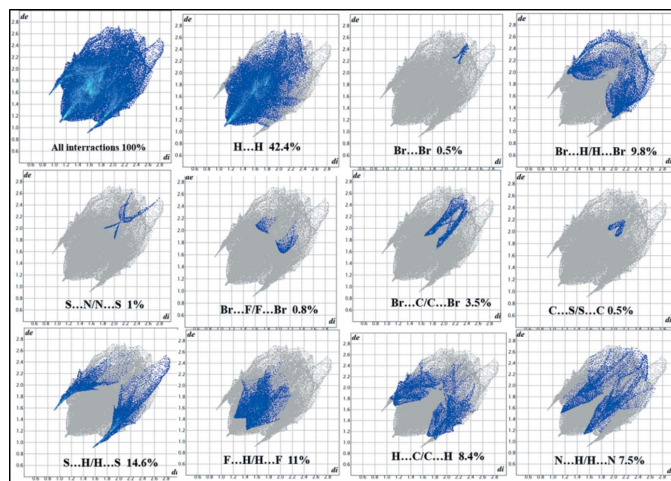


Figure 4
Fingerprint plots of the major interactions in compound **I**.

actions in the crystal structure, while the red regions over the shape-index surface are due to the presence of C—H \cdots π interactions.

The two-dimensional fingerprint maps for **I** provide some quantitative information about the individual contributions of the intermolecular interactions in the asymmetric unit (Figs. 4 and 5); the distinct spikes appearing in these plots help estimate the different interaction motifs in the crystal packing. As can be seen from Fig. 4, no C \cdots C interactions are present, which confirms the absence of π – π stacking in **I**. Globally, the highest contribution to the total Hirshfeld surface comes from the H \cdots H (42.4%) and S \cdots H/H \cdots S (14.6%) intermolecular contacts. This indicates that van der Waals forces have an important influence on the consolidation of the crystal struc-

Intermolecular interactions

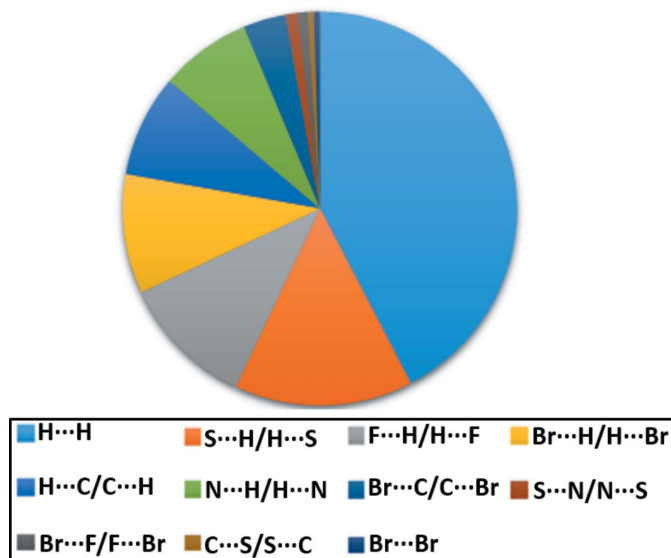


Figure 5
Relative contribution of the various intermolecular interactions in compound **I**.

ture. The other contacts contribute less to the Hirshfeld surfaces: F \cdots H/H \cdots F (11%), Br \cdots H/H \cdots Br (9.8%), H \cdots C/C \cdots H (8.4%), N \cdots H/H \cdots N (7.5%), Br \cdots C/C \cdots Br (3.5%), S \cdots N/N \cdots S (1%), Br \cdots Br (0.5%) and C \cdots S/S \cdots C (0.5%).

5. Database survey

A search of the Cambridge Structural Database (Version 2.0.1, last update, February 2019; Groom *et al.*, 2016) for adamantyl triazole-5(4*H*)-thione derivatives gave six hits containing a substituted triazole ring, namely: 3-(adamantan-1-yl)-4-benzyl-1*H*-1,2,4-triazole-5(4*H*)-thione (XOFLEL; Al-Omary *et al.*, 2014), with a benzyl substituent at position 4 of the 1,2,4-triazole ring; 3-(adamantan-1-yl)-4-(4-fluorophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (JAWZUF; Al-Shehri *et al.*, 2017), in which an F atom is the only substituent on the phenyl ring in the *para* position; 3-(adamantan-1-yl)-4-(prop-2-en-1-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione (LANXAB; Almutairi *et al.*, 2012), which exhibits a propenyl group, instead of a phenyl one, at position 4 of the triazole ring; 3-(adamantan-1-yl)-4-ethyl-1*H*-1,2,4-triazole-5(4*H*)-thione (ZAPJUX; El-Emam *et al.*, 2012), which has an ethyl group instead of a phenyl ring at position 4 of the triazole ring; 3-(adamantan-1-yl)-4-(4-chlorophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (WOTQUT; Al-Wabli *et al.*, 2015), with a Cl atom in the *para* position of the phenyl ring attached to the triazole moiety; 5-(adamantan-1-yl)-4-phenyl-2,4-dihydro-1,2,4-triazole-3-thione (WUMPUP; Nieger *et al.*, 2002), comprising a phenyl ring, without any substituents, at position 4 of the triazole ring. All of the substituents at position 4 of the planar triazole ring in these compounds are almost perpendicular to that ring, similar to the orientation of the phenyl substituent of the title compound. In the structures of all these compounds, the N—H \cdots S interactions play an important role in consolidating the crystal packing, along with C—H \cdots π interactions, when phenyl groups are present as substituents.

6. Synthesis and crystallization

All chemicals and solvents were used as purchased without further purification. The melting point was determined using an electrothermal digital melting-point apparatus and uncorrected. The NMR spectra were recorded at room temperature in DMSO- d_6 solution on a Bruker Ascend 700 NMR spectrometer. The title compound **I** was synthesized starting with adamantane-1-carbohydrazide **A** (El-Emam & Ibrahim, 1991) *via* the reaction with 2-bromo-4-fluorophenyl isothiocyanate **B** to yield the corresponding 4-(1-adamantylcarbonyl)-1-(2-bromo-4-fluorophenyl)-2-thiosemicarbazide **C**, which was then cyclized to the title compound **I** by heating in aqueous sodium hydroxide as outlined in Fig. 6.

2-Bromo-4-fluorophenyl isothiocyanate (2.32 g, 0.01 mol) was added to a solution of adamantane-1-carbohydrazide (1.94 g, 0.01 mol), in ethanol (10 mL), and the mixture was heated under reflux with stirring for one h. Ethanol was then distilled off *in vacuo* and an aqueous sodium hydroxide solution (10%, 15 mL) was added to the residue and the

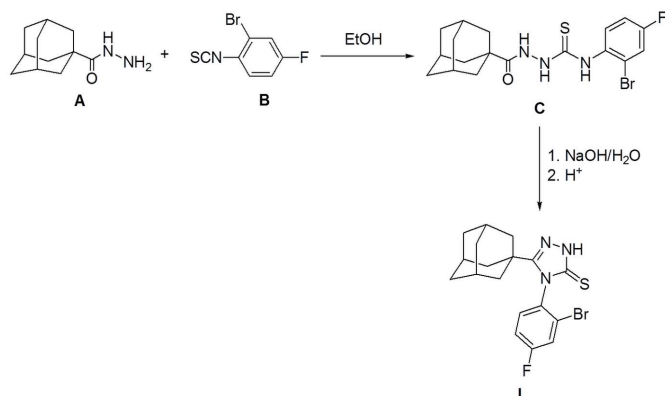


Figure 6
The reaction scheme yielding compound **I**.

mixture was heated under reflux for 4 h, then filtered hot. On cooling, the mixture was acidified with hydrochloric acid (pH 1–2) and the precipitated crude product was filtered, washed with water, dried and crystallized from an aqueous medium to yield 3.06 g (75%) of the title compound ($C_{18}H_{19}BrFN_3S$) as fine colourless crystals (m.p. 577–579 K). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the title compound in EtOH/ $CHCl_3$ (1:2, v/v) at room temperature. 1H NMR (DMSO- d_6 , 700.17 MHz): δ 1.47–1.71 (*m*, 9H, adamantane-H), 1.87–1.89 (*s*, 6H, adamantane-H), 7.47–7.52 (*m*, 1H, Ar-H), 7.69–7.71 (*m*, 1H, Ar-H), 7.87–7.90 (*m*, 1H, Ar-H), 13.86 (*s*, 1H, NH). ^{13}C NMR (DMSO- d_6 , 176.08 MHz): δ 27.92, 36.08, 36.57, 38.49 (adamantane-C), 115.0, 121.15, 131.65, 134.16, 135.21, 161.86 (Ar-C), 159.46 (triazole C=N), 169.41 (triazole C=S).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon and nitrogen-bound H atoms were placed in calculated positions (C–H 0.95 to 0.98 Å; N–H 0.86 Å) and were included in the refinement in the riding-model approximation, with $U_{iso}(H)$ set to 1.2 to $1.5U_{eq}(C,N)$. The structure was refined as a racemic twin [BASF: 0.50 (2)]. Four reflections ($\bar{4}$ 12 10, $\bar{4}$ 12 5, $\bar{4}$ 12 6 and $\bar{4}$ 12 9) were omitted from the last cycle of refinement owing to poor agreement.

Acknowledgements

Funding for this research was provided by: Financial support from the Spanish Ministerio de Economía y Competitividad (grant No. MAT2016-78155-C2-1-R); Gobierno del Principado de Asturias (award No. GRUPIN-IDI/2018/170).

Funding information

Funding for this research was provided by: Spanish Ministerio de Economía y Competitividad (grant No. MAT2016-78155-C2-1-R); Gobierno del Principado de Asturias (award No. GRUPIN-IDI/2018/170).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{19}BrFN_3S$
M_r	408.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	151
a, b, c (Å)	6.8473 (1), 12.5587 (2), 19.8090 (3)
V (Å ³)	1703.44 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	4.56
Crystal size (mm)	0.12 × 0.11 × 0.08
Data collection	
Diffractometer	Agilent Excalibur, Ruby, Gemini
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent 2014)
T_{min}, T_{max}	0.602, 0.694
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13191, 3572, 3244
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.081, 1.05
No. of reflections	3498
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.62, -0.36
Absolute structure	Flack (1983)
Absolute structure parameter	0.50 (2)

Computer programs: *SIR2011* (Burla *et al.*, 2012), *SHELXL* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *SCHAKAL* (Keller, 1989), *DIAMOND* (Brandenburg, 2006), *PARST* (Nardelli, 1995), *publCIF* (Westrip, 2010), *enCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2009).

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supporting information

Acta Cryst. (2020). E76, 162-166 [https://doi.org/10.1107/S2056989020000092]

Synthesis and crystal structure of 3-(adamantan-1-yl)-4-(2-bromo-4-fluorophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Computing details

Program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *SCHAKAL* (Keller, 1989), *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *PARST* (Nardelli, 1995), *publCIF* (Westrip, 2010), *enCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2009).

3-(Adamantan-1-yl)-4-(2-bromo-4-fluorophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

C₁₈H₁₉BrFN₃S

M_r = 408.32

Orthorhombic, *P*2₁2₁2₁

Hall symbol: P 2ac 2ab

a = 6.8473 (1) Å

b = 12.5587 (2) Å

c = 19.8090 (3) Å

V = 1703.44 (4) Å³

Z = 4

F(000) = 832

D_x = 1.592 Mg m⁻³

Cu *Kα* radiation, λ = 1.54184 Å

Cell parameters from 5537 reflections

θ = 4.2–74.6°

μ = 4.56 mm⁻¹

T = 151 K

Prism, colourless

0.12 × 0.11 × 0.08 mm

Data collection

Agilent Excalibur, Ruby, Gemini diffractometer

Graphite monochromator

Detector resolution: 10.2673 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Agilent 2014)

T_{min} = 0.602, *T_{max}* = 0.694

13191 measured reflections

3572 independent reflections

3244 reflections with *I* > 2σ(*I*)

R_{int} = 0.046

θ_{max} = 76.3°, θ_{min} = 4.2°

h = -8→8

k = -15→14

l = -23→24

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.035

wR(*F*²) = 0.081

S = 1.05

3498 reflections

218 parameters

0 restraints

0 constraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 1.0546P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.62 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack (1983)

Absolute structure parameter: 0.50 (2)

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. 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	-0.03402 (6)	0.64125 (3)	0.484532 (19)	0.03206 (11)
S1	-0.01416 (12)	0.31086 (6)	0.43635 (4)	0.02208 (17)
F1	0.6045 (3)	0.6344 (2)	0.34672 (10)	0.0370 (5)
N1	0.1505 (4)	0.4307 (2)	0.53736 (13)	0.0178 (6)
N3	-0.0802 (4)	0.3300 (2)	0.57154 (14)	0.0247 (7)
H3N	-0.1756	0.2854	0.572	0.03*
N2	-0.0120 (4)	0.3805 (2)	0.62852 (12)	0.0239 (6)
C4	0.4956 (5)	0.5857 (3)	0.39470 (15)	0.0251 (8)
C1	0.2724 (5)	0.4870 (3)	0.49068 (16)	0.0202 (6)
C5	0.3203 (5)	0.6311 (3)	0.41180 (15)	0.0240 (7)
H5	0.2778	0.6939	0.3917	0.029*
C7	0.0153 (4)	0.3567 (2)	0.51580 (14)	0.0195 (6)
C8	0.1279 (5)	0.4408 (3)	0.60780 (16)	0.0202 (7)
C11	0.2990 (5)	0.5637 (3)	0.77521 (16)	0.0256 (8)
H11	0.2373	0.5644	0.8198	0.031*
C2	0.4508 (5)	0.4436 (3)	0.47200 (15)	0.0238 (7)
H2	0.4943	0.3811	0.4922	0.029*
C17	0.4578 (5)	0.4462 (3)	0.65943 (16)	0.0242 (7)
H17A	0.4376	0.3733	0.6741	0.029*
H17B	0.5197	0.4446	0.6154	0.029*
C3	0.5643 (5)	0.4932 (3)	0.42340 (16)	0.0273 (8)
H3A	0.6839	0.4647	0.4105	0.033*
C6	0.2089 (5)	0.5793 (3)	0.46035 (16)	0.0212 (7)
C14	0.4279 (5)	0.6766 (3)	0.68164 (16)	0.0260 (8)
H14	0.4493	0.7499	0.6663	0.031*
C9	0.2594 (5)	0.5037 (3)	0.65435 (16)	0.0200 (7)
C12	0.4946 (6)	0.5054 (3)	0.77950 (15)	0.0280 (8)
H12A	0.5792	0.5411	0.8116	0.034*
H12B	0.4739	0.433	0.795	0.034*
C16	0.5909 (5)	0.5041 (3)	0.70996 (17)	0.0269 (8)
H16	0.7167	0.4671	0.7127	0.032*

C10	0.1647 (5)	0.5061 (3)	0.72489 (16)	0.0254 (8)
H10A	0.04	0.5425	0.7225	0.031*
H10B	0.1414	0.4338	0.7402	0.031*
C13	0.3326 (6)	0.6782 (3)	0.75170 (17)	0.0271 (8)
H13A	0.4168	0.715	0.7834	0.033*
H13B	0.2091	0.7159	0.7496	0.033*
C18	0.2933 (5)	0.6190 (3)	0.63142 (16)	0.0245 (8)
H18A	0.1692	0.656	0.6287	0.029*
H18B	0.3523	0.6193	0.5869	0.029*
C15	0.6237 (5)	0.6188 (3)	0.68563 (18)	0.0298 (9)
H15A	0.7097	0.6558	0.7167	0.036*
H15B	0.6852	0.6182	0.6415	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02922 (18)	0.0329 (2)	0.03404 (17)	0.01027 (18)	-0.00194 (16)	0.00029 (16)
S1	0.0243 (4)	0.0216 (4)	0.0204 (3)	-0.0005 (4)	-0.0022 (3)	-0.0017 (3)
F1	0.0388 (12)	0.0395 (14)	0.0329 (11)	-0.0117 (12)	0.0067 (9)	0.0123 (11)
N1	0.0206 (14)	0.0149 (14)	0.0178 (12)	-0.0008 (12)	-0.0001 (10)	-0.0009 (10)
N3	0.0226 (15)	0.0257 (16)	0.0260 (14)	-0.0095 (12)	0.0020 (11)	-0.0048 (11)
N2	0.0234 (16)	0.0259 (16)	0.0225 (12)	-0.0050 (13)	0.0030 (11)	-0.0077 (10)
C4	0.030 (2)	0.0235 (17)	0.0221 (14)	-0.0089 (16)	0.0000 (14)	0.0023 (12)
C1	0.0212 (15)	0.0185 (16)	0.0210 (14)	-0.0039 (13)	-0.0024 (13)	0.0008 (13)
C5	0.0306 (18)	0.0186 (18)	0.0227 (15)	-0.0049 (17)	-0.0059 (13)	0.0024 (14)
C7	0.0179 (14)	0.0171 (14)	0.0235 (13)	0.0035 (15)	-0.0034 (13)	0.0020 (13)
C8	0.0205 (16)	0.0184 (18)	0.0218 (15)	-0.0009 (14)	-0.0008 (12)	-0.0014 (13)
C11	0.0280 (18)	0.030 (2)	0.0188 (15)	-0.0016 (16)	0.0002 (14)	-0.0028 (14)
C2	0.0253 (16)	0.0234 (17)	0.0226 (15)	-0.0003 (16)	-0.0038 (14)	0.0003 (12)
C17	0.0240 (16)	0.0225 (17)	0.0263 (15)	0.0027 (16)	-0.0016 (15)	-0.0050 (13)
C3	0.0251 (19)	0.031 (2)	0.0262 (16)	-0.0038 (16)	0.0019 (14)	-0.0032 (14)
C6	0.0200 (16)	0.0182 (17)	0.0253 (15)	0.0037 (14)	-0.0033 (13)	-0.0059 (13)
C14	0.035 (2)	0.0182 (17)	0.0249 (16)	-0.0062 (15)	-0.0046 (14)	0.0012 (13)
C9	0.0212 (17)	0.0181 (17)	0.0207 (15)	-0.0021 (14)	0.0007 (12)	-0.0029 (13)
C12	0.037 (2)	0.0249 (18)	0.0226 (14)	-0.0001 (17)	-0.0091 (15)	0.0019 (12)
C16	0.0194 (18)	0.031 (2)	0.0301 (17)	0.0041 (15)	-0.0045 (13)	-0.0030 (15)
C10	0.0231 (18)	0.029 (2)	0.0243 (16)	-0.0059 (16)	0.0038 (13)	-0.0030 (15)
C13	0.0315 (19)	0.023 (2)	0.0266 (17)	0.0010 (16)	-0.0042 (14)	-0.0079 (14)
C18	0.0268 (18)	0.025 (2)	0.0220 (15)	-0.0018 (15)	-0.0063 (13)	0.0010 (13)
C15	0.0246 (18)	0.035 (3)	0.0296 (17)	-0.0081 (17)	-0.0017 (14)	0.0007 (16)

Geometric parameters (Å, °)

Br1—C6	1.898 (3)	C17—C9	1.542 (5)
S1—C7	1.688 (3)	C17—H17A	0.97
F1—C4	1.355 (4)	C17—H17B	0.97
N1—C7	1.379 (4)	C3—H3A	0.93
N1—C8	1.410 (4)	C14—C15	1.526 (5)

N1—C1	1.433 (4)	C14—C13	1.534 (5)
N3—C7	1.327 (4)	C14—C18	1.537 (5)
N3—N2	1.377 (4)	C14—H14	0.98
N3—H3N	0.86	C9—C18	1.535 (5)
N2—C8	1.288 (4)	C9—C10	1.541 (4)
C4—C5	1.371 (5)	C12—C16	1.527 (5)
C4—C3	1.376 (5)	C12—H12A	0.97
C1—C6	1.377 (5)	C12—H12B	0.97
C1—C2	1.387 (5)	C16—C15	1.536 (5)
C5—C6	1.389 (5)	C16—H16	0.98
C5—H5	0.93	C10—H10A	0.97
C8—C9	1.512 (5)	C10—H10B	0.97
C11—C12	1.529 (5)	C13—H13A	0.97
C11—C13	1.529 (5)	C13—H13B	0.97
C11—C10	1.537 (5)	C18—H18A	0.97
C11—H11	0.98	C18—H18B	0.97
C2—C3	1.385 (5)	C15—H15A	0.97
C2—H2	0.93	C15—H15B	0.97
C17—C16	1.537 (5)		
C7—N1—C8	107.1 (3)	C15—C14—H14	109.3
C7—N1—C1	121.6 (3)	C13—C14—H14	109.3
C8—N1—C1	131.2 (3)	C18—C14—H14	109.3
C7—N3—N2	113.5 (3)	C8—C9—C18	113.7 (3)
C7—N3—H3N	123.3	C8—C9—C10	108.2 (3)
N2—N3—H3N	123.3	C18—C9—C10	108.3 (3)
C8—N2—N3	105.2 (3)	C8—C9—C17	108.6 (3)
F1—C4—C5	117.9 (3)	C18—C9—C17	109.2 (3)
F1—C4—C3	118.9 (3)	C10—C9—C17	108.7 (3)
C5—C4—C3	123.2 (3)	C16—C12—C11	109.5 (3)
C6—C1—C2	119.5 (3)	C16—C12—H12A	109.8
C6—C1—N1	120.9 (3)	C11—C12—H12A	109.8
C2—C1—N1	119.4 (3)	C16—C12—H12B	109.8
C4—C5—C6	117.2 (3)	C11—C12—H12B	109.8
C4—C5—H5	121.4	H12A—C12—H12B	108.2
C6—C5—H5	121.4	C12—C16—C15	109.6 (3)
N3—C7—N1	104.1 (2)	C12—C16—C17	109.7 (3)
N3—C7—S1	129.1 (2)	C15—C16—C17	109.0 (3)
N1—C7—S1	126.8 (2)	C12—C16—H16	109.5
N2—C8—N1	110.1 (3)	C15—C16—H16	109.5
N2—C8—C9	123.8 (3)	C17—C16—H16	109.5
N1—C8—C9	125.8 (3)	C11—C10—C9	110.2 (3)
C12—C11—C13	109.6 (3)	C11—C10—H10A	109.6
C12—C11—C10	109.5 (3)	C9—C10—H10A	109.6
C13—C11—C10	109.6 (3)	C11—C10—H10B	109.6
C12—C11—H11	109.4	C9—C10—H10B	109.6
C13—C11—H11	109.4	H10A—C10—H10B	108.1
C10—C11—H11	109.4	C11—C13—C14	109.1 (3)

C3—C2—C1	120.2 (3)	C11—C13—H13A	109.9
C3—C2—H2	119.9	C14—C13—H13A	109.9
C1—C2—H2	119.9	C11—C13—H13B	109.9
C16—C17—C9	110.1 (3)	C14—C13—H13B	109.9
C16—C17—H17A	109.6	H13A—C13—H13B	108.3
C9—C17—H17A	109.6	C9—C18—C14	110.1 (3)
C16—C17—H17B	109.6	C9—C18—H18A	109.6
C9—C17—H17B	109.6	C14—C18—H18A	109.6
H17A—C17—H17B	108.2	C9—C18—H18B	109.6
C4—C3—C2	118.4 (3)	C14—C18—H18B	109.6
C4—C3—H3A	120.8	H18A—C18—H18B	108.2
C2—C3—H3A	120.8	C14—C15—C16	109.5 (3)
C1—C6—C5	121.5 (3)	C14—C15—H15A	109.8
C1—C6—Br1	120.8 (3)	C16—C15—H15A	109.8
C5—C6—Br1	117.7 (3)	C14—C15—H15B	109.8
C15—C14—C13	109.5 (3)	C16—C15—H15B	109.8
C15—C14—C18	109.7 (3)	H15A—C15—H15B	108.2
C13—C14—C18	109.7 (3)		

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C1—C2 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H3N \cdots S1 ⁱ	0.86	2.62	3.461 (3)	166
C2—H2 \cdots S1 ⁱⁱ	0.93	2.8	3.683 (3)	160
C11—H11 \cdots Cg2 ⁱⁱⁱ	0.98	2.86	3.757 (4)	152

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