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Crystal structure and Hirshfeld surface analysis of 1-(2-fluorophenyl)-1*H*-tetrazole-5(4*H*)-thione

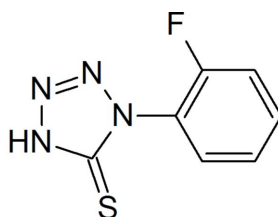
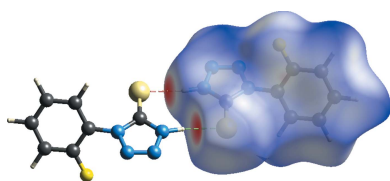
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In the crystal of the title compound, C₇H₅FN₄S, the molecules are non-planar, with dihedral angle formed by least-squares planes of tetrazole and benzene rings of 59.94 (8)°. The crystal packing is formed by N—H···S hydrogen bonds, which link the molecules into centrosymmetric dimers with an R₂²(8) ring motif, and by the offset face-to-face π - π stacking interactions between the benzene rings, which join the dimers into layers parallel to (100). The Hirshfeld surface analysis shows that the most important contributions to the surface contacts are from N···H/H···N (21.9%), S···H/H···S (21.1%), H···H (14.6%), F···H/H···F (11.8%) and C···H/H···C (9.5%) interactions.

1. Chemical context

Tetrazoles as an important class of five-membered heterocyclic compounds have been known for over a hundred years. The most common synthetic approach to construct tetrazoles, based on the reaction of nitriles with hydrazoic acid, was first discovered by Hantzsch & Vagt (1901). Up to know, most synthetic protocols comprise the cycloaddition of nitriles, thiocyanates or isothiocyanates with an azide moiety, under different conditions. Tetrazole derivatives have found a broad range of applications in medicinal chemistry (Wang *et al.*, 2019; Gao *et al.*, 2019; Arulmozhi *et al.*, 2017), coordination chemistry (Askerov *et al.*, 2018; Askerov *et al.*, 2019*a,b*; Aromí *et al.*, 2011) and material science (Frija *et al.*, 2010; Lv *et al.*, 2006). Numerous tetrazole-based synthetic compounds such as tomelukast, cefazolin, losartan, valsartan and alfentanil have already been used in medicinal practice.



As a result of the considerable interest in this field, significant developments in the synthesis of tetrazoles have been attained, which were recently reviewed (Neochoritis *et al.*, 2019). As a further study of the chemistry of tetrazoles, herein we report the crystal structure and Hirshfeld surface analysis of the title compound.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H4\cdots S1^i$	0.90 (2)	2.35 (2)	3.2456 (12)	173.2 (18)

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

2. Structural commentary

The molecule of the title compound (Fig. 1) is non-planar. The five-membered 4-dihydro-5*H*-tetrazole ring (N1–N4/C5) is essentially planar, with a largest deviation of 0.005 (1) Å for N3. The dihedral angle between the mean planes of the tetrazole and benzene rings is 59.94 (8)°. The bond dimensions are typical of similar compounds, with a distinct N2=N3 double bond.

3. Supramolecular features

In the crystal, molecules are linked by pairs of N–H⋯S hydrogen bonds, forming centrosymmetric dimers with an $R_2^2(8)$ ring motif (see Fig. 2 and Table 1). The dimers are linked by the offset face-to-face π – π stacking interactions between the benzene rings, which are characterized by intercentroid distances of 3.8963 (9) and 3.8964 (9) Å, and centroid-to-plane distances of 3.4589 (6) and 3.4578 (6) Å (Fig. 2). Neighbouring molecules within the stack are related by the *c* glide plane. The hydrogen bonds and stacking interactions link the molecules into layers parallel to (100). Other short intermolecular contacts are collected in Table 2.

4. Hirshfeld surface analysis

In order to investigate the intermolecular interactions in the crystal structure of the title compound in a visual manner, Hirshfeld surfaces (McKinnon *et al.*, 2007) and their associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were generated using *CrystalExplorer17* (Turner *et al.*, 2017). The shorter and longer contacts are indicated as red and blue spots, respectively, on the Hirshfeld surfaces, and contacts with distances approximately equal to

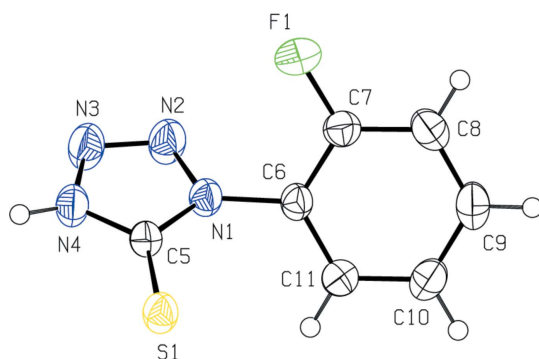
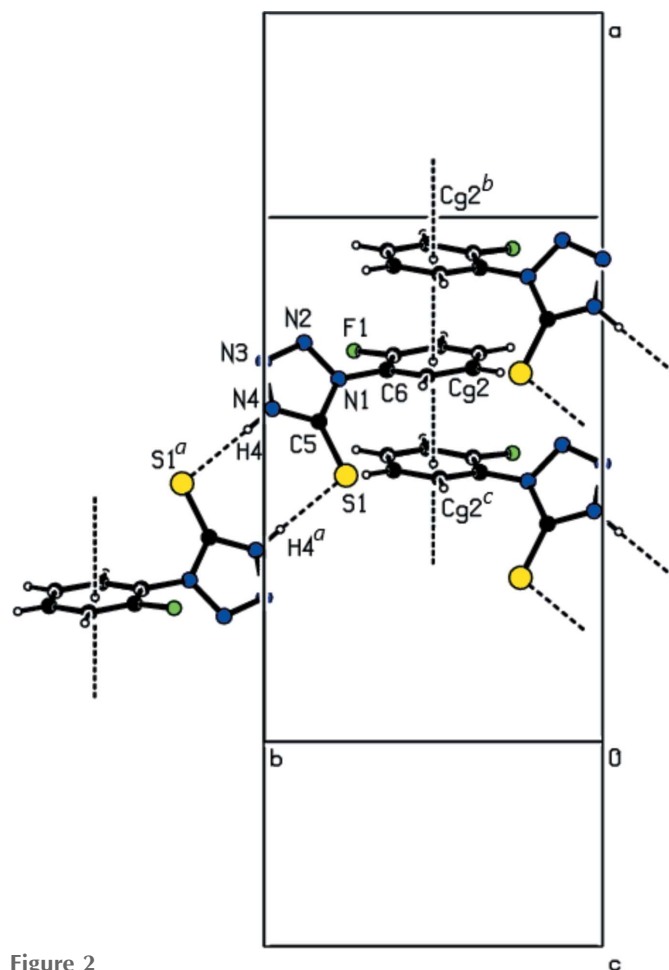
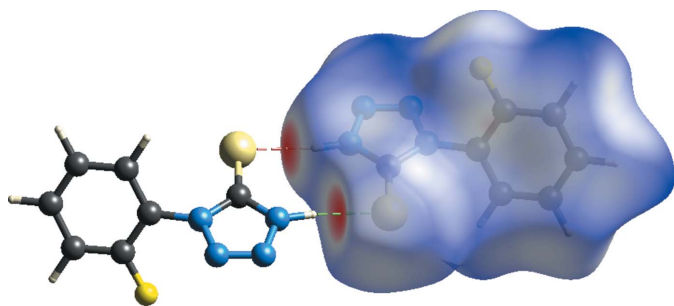

Figure 1
 The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

Table 2
 Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
$S1\cdots S1$	3.7741 (6)	$1 - x, y, \frac{3}{2} - z$
$C5\cdots S1$	3.6367 (13)	$1 - x, y, \frac{1}{2} - z$
$H4\cdots S1$	2.35	$1 - x, 2 - y, 1 - z$
$H10A\cdots S1$	3.18	$1 - x, 1 - y, 1 - z$
$S1\cdots H10A$	3.04	$x, 1 - y, \frac{1}{2} + z$
$F1\cdots H8A$	2.63	$\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$
$F1\cdots F1$	3.0330 (15)	$\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$
$N3\cdots H10A$	2.82	$x, 1 + y, z$
$N3\cdots C5$	3.38	$x, 2 - y, -\frac{1}{2} + z$

the sum of the van der Waals radii are represented as white spots. The contribution of interatomic contacts (Table 2) to the d_{norm} surface of the title compound is shown in Fig. 3. In Fig. 4, red and blue triangles can be seen on the shape-index surface, which indicate the presence of π – π stacking interactions in the crystal structure. Analysis of the two-dimensional fingerprint plots (Fig. 5) reveals that N⋯H/H⋯N (21.9%) and S⋯H/H⋯S (21.1%) contacts (*i.e.* N–H⋯S) are the major contri-


Figure 2
 Crystal packing of the title compound viewed along the *a*-axis direction. Dashed lines indicate the N–H⋯S hydrogen bonds, which form centrosymmetric dimers with an $R_2^2(8)$ ring motif, and the face-to-face π – π stacking interactions, which connect the dimers into layers parallel to (100).

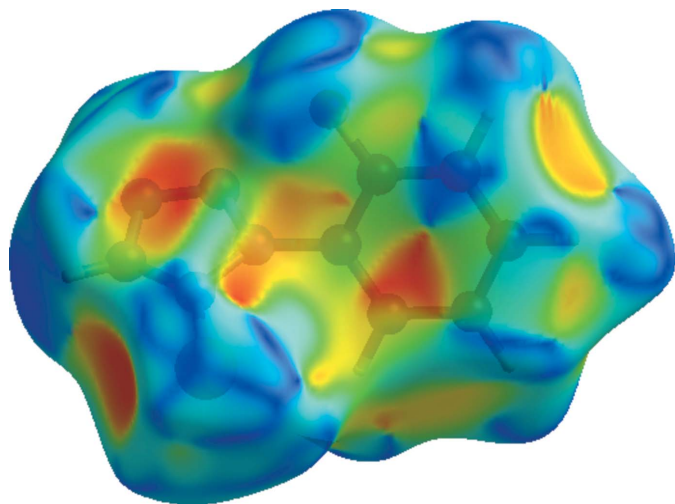

Figure 3

A view of the three-dimensional Hirshfeld surface for the title molecule, plotted over d_{norm} ranging from -0.4612 to 1.2843 a.u. A dimer formed by $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds is shown.

butors to the Hirshfeld surface, while $\text{H}\cdots\text{H}$ (14.6%), $\text{F}\cdots\text{H}/\text{H}\cdots\text{F}$ (11.8%) and $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ (9.5%) contacts make a less significant contribution. The contribution of the $\text{C}\cdots\text{C}$ (6.6%) (*i.e.* π - π stacking) contacts and other contacts such as $\text{N}\cdots\text{N}$ (2.8%), $\text{F}\cdots\text{C}/\text{C}\cdots\text{F}$ (2.4%), $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$ (2.4%), $\text{F}\cdots\text{N}/\text{N}\cdots\text{F}$ (1.7%), $\text{S}\cdots\text{N}/\text{N}\cdots\text{S}$ (1.7%), $\text{S}\cdots\text{C}/\text{C}\cdots\text{S}$ (1.7%), $\text{F}\cdots\text{F}$ (1.5%) and $\text{S}\cdots\text{S}$ (0.4%) make a small contribution to the overall Hirshfeld surface.

5. Database survey

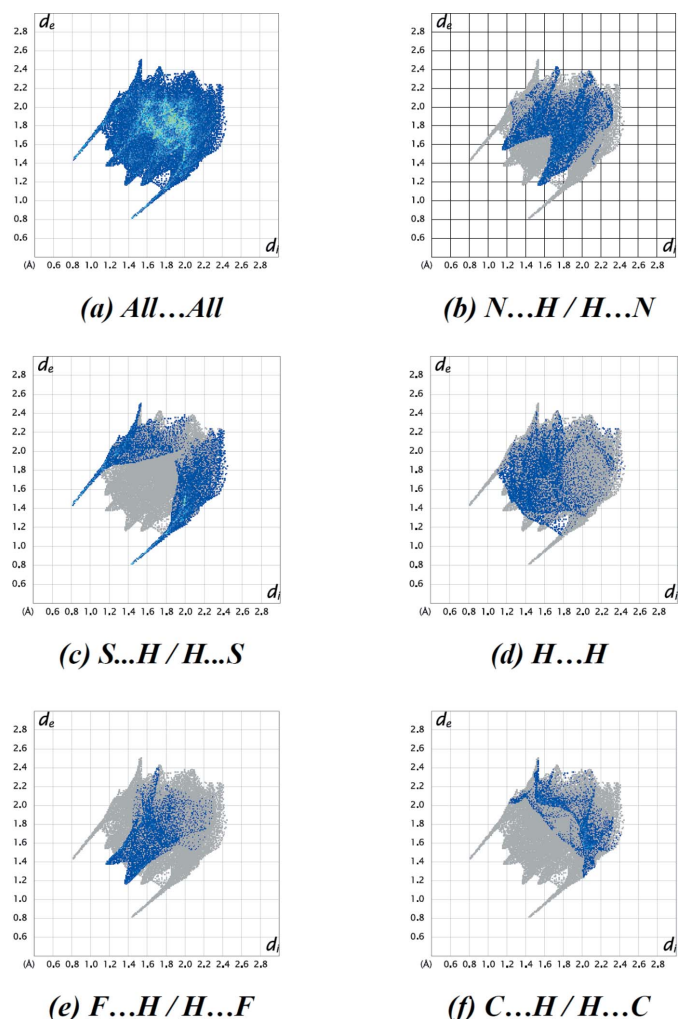
A search of the Cambridge Crystallographic Database (CSD version 5.40, update of September 2019; Groom *et al.*, 2016) yielded nine entries closely related to the title compound, *viz.* 1-(4-fluorophenyl)-4,4,6-trimethyl-3,4-dihydropyrimidine-2(1*H*)-thione (CSD refcode ASEHIR; Kadir *et al.*, 2016), 3-(adamantan-1-yl)-4-(4-fluorophenyl)-1-[(4-phenylpiperazin-1-yl)methyl]-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (ZEFKED; Al-Alshaikh *et al.*, 2017), 3-(adamantan-1-yl)-4-(4-fluorophenyl)-1-[[4-(2-methoxyphenyl)piperazin-1-yl]-methyl]-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (ZEFKAZ; Al-Alshaikh *et al.*, 2017), 3-(adamantan-1-yl)-4-(2-bromo-4-fluorophenyl)-


Figure 4

Hirshfeld surface of the title molecule plotted over shape-index.

1*H*-1,2,4-triazole-5(4*H*)-thione (ZOZNEK; Abdelrazeq *et al.*, 2020), 2-fluoro-*N*-(3-(methylsulfanyl)-1*H*-1,2,4-triazol-5-yl)-benzamide (MITMOU; Moreno-Fuquen *et al.*, 2019), (5-amino-3-(methylsulfanyl)-1*H*-1,2,4-triazol-1-yl)(2-fluorophenyl)methanone (MITMIO; Moreno-Fuquen *et al.*, 2019), 4-(benzo[*b*]thiophen-2-yl)-5-(3,4,5-trimethoxyphenyl)-2*H*-1,2,3-triazole (PONWIA; Penthala *et al.*, 2014), 4-(benzo[*b*]thiophen-2-yl)-2-methyl-5-(3,4,5-trimethoxyphenyl)-2*H*-1,2,3-triazole (PONWOG; Penthala *et al.*, 2014), (*E*)-3-(4-fluorophenyl)-1-[1-(4-fluorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (MESTAI; El-Hiti *et al.*, 2018), 4-amino-3-methyl-5-(*p*-tolyl)-4*H*-1,2,4-triazole (JESTOR; Şahin *et al.*, 2006), 4-amino-3-methyl-5-phenyl-4*H*-1,2,4-triazole (JESTUX; Şahin *et al.*, 2006), and 2-phenyl-4,5-dianilino-2*H*-1,2,3-triazole (PANTZL10; Harlow *et al.*, 1977).

In the crystal of ASEHIR, pairs of molecules related by the twofold rotation axis are linked by the $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, forming dimers.


Figure 5

A view of two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, (c) $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$, (d) $\text{H}\cdots\text{H}$, (e) $\text{F}\cdots\text{H}/\text{H}\cdots\text{F}$ and (f) $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

The crystal structure of ZEFKED shows pairs of C—H...F hydrogen bonds forming inversion dimers, while in the crystal of ZEFKAZ, in addition to the C—H...F hydrogen bonds that generate chains parallel to the *b* axis, there are C—H... π interactions that link the chains to form layers parallel to the *ab* plane.

In the crystal of ZOZNEK, 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.

In the crystal structure of MITMOU, the supramolecular assembly is formed mainly by (N,C)—H... π (N,O) hydrogen-bond interactions. Initially, strong N—H...N hydrogen bonds link pairs of inversion-related molecules that act as slabs of infinite chains running along the [100] direction connected by a C—H...O hydrogen bond. Along the [010] direction, neighbouring chains are further connected by weak π – π interactions between two arene rings of adjacent molecules.

The crystal structure of MITMIO is built by a combination of strong N—H...O and N—H...N hydrogen bonds, which form chains of molecules running along the [100] direction. Parallel inversion-related chains of molecules are further connected by weaker C—H...O interactions to build the molecular architecture along the [001] direction. Weak C—H...N interactions connect the molecules in order to complete the three-dimensional structure along the [010] direction.

In the crystal of PONWIA, the molecules are linked into chains by N—H...O hydrogen bonds with $R_1^2(5)$ ring motifs. After the *N*-methylation of the PONWIA molecule, no hydrogen-bonding interactions were observed for structure PONWOG. The crystal structure of PONWOG shows a disorder due to a 180° flip of the benzothiophene ring system.

In the crystal of MESTAI, the asymmetric unit comprises two molecules with similar conformations. In the crystal, weak C—H...F interactions form chains of molecules and the chains are stacked to form layers parallel to (101).

In JESTOR, molecules are linked principally by N—H...N hydrogen bonds involving the amino NH₂ group and a triazole N atom, forming $R_4^4(20)$ and $R_4^2(10)$ rings that combine to give a three-dimensional network of molecules. The hydrogen bonding is supported by two different C—H... π interactions from the tolyl ring to either a triazole ring or a tolyl ring in a neighboring molecule. In JESTUX, intermolecular hydrogen bonds and C—H... π interactions generate $R_4^3(15)$ and $R_4^4(21)$ rings.

6. Synthesis and crystallization

To a solution of NaN₃ (29 mmol) in 50 mL of H₂O 2-fluorophenylisothiocyanate (19.6 mmol) was added at 293 K. The reaction mixture was boiled for 2 h, cooled to 293 K; then the aqueous solution was filtered from undissolved impurities and a 10% aqueous solution of HCl was added to it with stirring to pH = 2. The precipitate of the title compound was

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₇ H ₅ FN ₄ S
<i>M_r</i>	196.21
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.5593 (11), 9.2849 (5), 7.7927 (4)
β (°)	104.009 (1)
<i>V</i> (Å ³)	1653.92 (15)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.36
Crystal size (mm)	0.23 × 0.15 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.690, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	9005, 2406, 2135
<i>R_{int}</i>	0.017
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.713
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.036, 0.098, 1.00
No. of reflections	2406
No. of parameters	122
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.29, -0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2003), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

filtered off, washed with water, and then the product was recrystallized from ethanol.

1-(2-Fluorophenyl)-1*H*-tetrazole-5(4*H*)-thione: yield 72% as white powder, m.p. 426 K. Analysis calculated for C₇H₅FN₄S (%): C 42.85, H 2.57, N 28.56. Found (%): C 42.62, H 2.66, N 28.59. ¹H NMR (400.00 MHz, DMSO-*d*₆): δ = 7.73 (*m*, 1H), 7.68 (*m*, 1H), 7.55 (*t*, 1H), 7.45 (*t*, 1H). ¹³C NMR (100.60 MHz, DMSO-*d*₆): δ = 162.76 (C=S), 156.39 (C-F), [137.33 (C-N, Ar), 128.76, 127.08, 124.94, 114.88 (4CH, Ar)].

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were placed in calculated positions (0.93 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H atom was located in a difference map and refined isotropically.

References

- Abdelrazeq, A. S., Ghabbour, H. A., El-Emam, A. A., Osman, D. A. & Garcia-Granda, S. (2020). *Acta Cryst.* **E76**, 162–166.
- Al-Alshaiikh, M. A., Al-Mutairi, A. A., Ghabbour, H. A., El-Emam, A. A., Abdelbaky, M. S. M. & Garcia-Granda, S. (2017). *Acta Cryst.* **E73**, 1135–1139.
- Aromí, G., Barrios, L. A., Roubeau, O. & Gamez, P. (2011). *Coord. Chem. Rev.* **255**, 485–546.
- Arulmozhi, R., Abirami, N. & Helen, K. P. (2017). *Int. J. Pharm. Sci. Rev. Res.* **21**, 110–114.

- Askerov, R. K., Magerramov, A. M., Osmanov, V. K., Baranov, E. V., Borisova, G. N. & Borisov, A. V. (2019b). *Russ. J. Coord. Chem.* **45**, 555–562.
- Askerov, R. K., Magerramov, A. M., Osmanov, V. K., Baranov, E. V., Borisova, G. N., Samsonova, A. D. & Borisov, A. V. (2019a). *Russ. J. Coord. Chem.* **45**, 112–118.
- Askerov, R. K., Maharramov, A. M., Osmanov, V. K., Baranov, E. V., Borisova, G. N., Dorovatovskii, P. V., Khrustalev, V. N. & Borisov, A. V. (2018). *J. Struct. Chem.* **59**, 1658–1663.
- Bruker (2003). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- El-Hiti, G. A., Abdel-Wahab, B. F., Alotaibi, M. H., Hegazy, A. S. & Kariuki, B. M. (2018). *IUCrData*, **3**, x171841.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Frija, L. M. T., Ismael, A. & Cristiano, M. L. S. (2010). *Molecules*, **15**, 3757–3774.
- Gao, C., Chang, L., Xu, Z., Yan, X.-F., Ding, C., Zhao, F., Wu, X. & Feng, L.-S. (2019). *Eur. J. Med. Chem.* **163**, 404–412.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hantzsch, A. & Vagt, A. (1901). *Justus Liebigs Ann. Chem.* **314**, 339–369.
- Harlow, R. L., Brown, S. B., Dewar, M. J. S. & Simonsen, S. H. (1977). *Acta Cryst.* **B33**, 3423–3428.
- Kadir, A., Abd Malek, N. A., Mohd Zaki, H., Hasbullah, S. A. & Yamin, B. M. (2016). *IUCrData*, **1**, x161189.
- Lv, F., Liu, Y., Zou, J., Zhang, D. & Yao, Z. (2006). *Dyes Pigments*, **68**, 211–216.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Moreno-Fuquen, R., Arango-Daraviña, K., Becerra, D., Castillo, J.-C., Kennedy, A. R. & Macías, M. A. (2019). *Acta Cryst.* **C75**, 359–371.
- Neochoritis, C. G., Zhao, T. & Dömling, A. (2019). *Chem. Rev.* **119**, 1970–2042.
- Penthala, N. R., Madadi, N. R., Bommagani, S., Parkin, S. & Crooks, P. A. (2014). *Acta Cryst.* **E70**, 392–395.
- Şahin, O., Büyükgüngör, O., Şaşmaz, S., Gümrükçüoğlu, N. & Kantar, C. (2006). *Acta Cryst.* **C62**, o643–o646.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & McKinnon, J. J. (2002). *CrystEngComm*, **4**, 378–392.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.
- Wang, S.-Q., Wang, Y.-F. & Xu, Z. (2019). *Eur. J. Med. Chem.* **170**, 225–234.

supporting information

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Crystal structure and Hirshfeld surface analysis of 1-(2-fluorophenyl)-1*H*-tetrazole-5(4*H*)-thione

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Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

1-(2-Fluorophenyl)-1*H*-tetrazole-5(4*H*)-thione

Crystal data

$C_7H_5FN_4S$

$M_r = 196.21$

Monoclinic, *C2/c*

$a = 23.5593$ (11) Å

$b = 9.2849$ (5) Å

$c = 7.7927$ (4) Å

$\beta = 104.009$ (1)°

$V = 1653.92$ (15) Å³

$Z = 8$

$F(000) = 800$

$D_x = 1.576$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 4417 reflections

$\theta = 2.4$ – 30.5 °

$\mu = 0.36$ mm⁻¹

$T = 296$ K

Prism, colourless

$0.23 \times 0.15 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2003)

$T_{\min} = 0.690$, $T_{\max} = 0.746$

9005 measured reflections

2406 independent reflections

2135 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 30.5$ °, $\theta_{\min} = 1.8$ °

$h = -32 \rightarrow 33$

$k = -13 \rightarrow 13$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.098$

$S = 1.00$

2406 reflections

122 parameters

0 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 1.1614P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.51038 (2)	0.75776 (4)	0.51736 (5)	0.03900 (12)
F1	0.71634 (4)	0.73413 (10)	0.64199 (14)	0.0536 (3)
N1	0.61196 (5)	0.77955 (12)	0.40738 (16)	0.0346 (2)
N2	0.64339 (6)	0.88176 (13)	0.3424 (2)	0.0480 (3)
N3	0.61568 (6)	1.00050 (13)	0.3346 (2)	0.0494 (3)
N4	0.56649 (5)	0.97577 (12)	0.39123 (17)	0.0399 (3)
H4	0.5428 (9)	1.048 (2)	0.408 (3)	0.060 (5)*
C5	0.56255 (5)	0.83768 (13)	0.43970 (17)	0.0320 (2)
C6	0.63424 (5)	0.63719 (13)	0.44289 (17)	0.0314 (2)
C7	0.68772 (6)	0.61740 (14)	0.56178 (18)	0.0361 (3)
C8	0.71115 (6)	0.48238 (16)	0.6014 (2)	0.0434 (3)
H8A	0.747433	0.470495	0.680048	0.052*
C9	0.67955 (7)	0.36465 (16)	0.5217 (2)	0.0444 (3)
H9A	0.694563	0.272435	0.547932	0.053*
C10	0.62584 (7)	0.38250 (15)	0.4034 (2)	0.0419 (3)
H10A	0.604979	0.302279	0.351172	0.050*
C11	0.60297 (6)	0.51874 (14)	0.36219 (19)	0.0369 (3)
H11A	0.567110	0.530830	0.281472	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.03642 (19)	0.03299 (18)	0.0519 (2)	0.00355 (12)	0.01903 (15)	0.00288 (13)
F1	0.0467 (5)	0.0476 (5)	0.0603 (6)	-0.0097 (4)	0.0012 (4)	-0.0104 (4)
N1	0.0316 (5)	0.0285 (5)	0.0465 (6)	0.0026 (4)	0.0148 (4)	0.0020 (4)
N2	0.0431 (6)	0.0347 (6)	0.0728 (9)	0.0013 (5)	0.0267 (6)	0.0084 (6)
N3	0.0476 (7)	0.0330 (6)	0.0737 (9)	0.0031 (5)	0.0266 (6)	0.0085 (6)
N4	0.0404 (6)	0.0291 (5)	0.0529 (7)	0.0056 (4)	0.0165 (5)	0.0035 (5)
C5	0.0314 (5)	0.0287 (6)	0.0356 (6)	0.0034 (4)	0.0076 (5)	-0.0012 (4)
C6	0.0311 (5)	0.0277 (5)	0.0378 (6)	0.0035 (4)	0.0126 (5)	0.0009 (4)
C7	0.0334 (6)	0.0351 (6)	0.0400 (6)	-0.0017 (5)	0.0095 (5)	-0.0028 (5)
C8	0.0350 (6)	0.0463 (8)	0.0475 (8)	0.0082 (6)	0.0072 (6)	0.0077 (6)
C9	0.0486 (8)	0.0338 (7)	0.0548 (8)	0.0104 (6)	0.0202 (6)	0.0088 (6)
C10	0.0472 (7)	0.0307 (6)	0.0508 (8)	-0.0028 (5)	0.0178 (6)	-0.0032 (6)
C11	0.0345 (6)	0.0338 (6)	0.0421 (7)	-0.0007 (5)	0.0086 (5)	-0.0014 (5)

Geometric parameters (Å, °)

S1—C5	1.6696 (13)	C6—C11	1.3868 (18)
F1—C7	1.3476 (15)	C7—C8	1.3745 (19)
N1—C5	1.3608 (15)	C8—C9	1.382 (2)
N1—N2	1.3735 (16)	C8—H8A	0.9300
N1—C6	1.4244 (16)	C9—C10	1.384 (2)
N2—N3	1.2752 (16)	C9—H9A	0.9300
N3—N4	1.3558 (17)	C10—C11	1.3818 (19)
N4—C5	1.3462 (17)	C10—H10A	0.9300
N4—H4	0.90 (2)	C11—H11A	0.9300
C6—C7	1.3836 (18)		
C5—N1—N2	110.84 (11)	F1—C7—C6	118.43 (12)
C5—N1—C6	128.58 (11)	C8—C7—C6	121.51 (12)
N2—N1—C6	120.44 (10)	C7—C8—C9	118.49 (13)
N3—N2—N1	107.44 (11)	C7—C8—H8A	120.8
N2—N3—N4	107.81 (11)	C9—C8—H8A	120.8
C5—N4—N3	112.04 (11)	C8—C9—C10	120.72 (13)
C5—N4—H4	125.3 (13)	C8—C9—H9A	119.6
N3—N4—H4	122.1 (13)	C10—C9—H9A	119.6
N4—C5—N1	101.86 (11)	C11—C10—C9	120.44 (13)
N4—C5—S1	129.19 (10)	C11—C10—H10A	119.8
N1—C5—S1	128.94 (10)	C9—C10—H10A	119.8
C7—C6—C11	119.73 (12)	C10—C11—C6	119.10 (13)
C7—C6—N1	119.10 (11)	C10—C11—H11A	120.4
C11—C6—N1	121.17 (11)	C6—C11—H11A	120.4
F1—C7—C8	120.05 (12)		
C5—N1—N2—N3	0.45 (18)	N2—N1—C6—C11	-122.21 (15)
C6—N1—N2—N3	-175.58 (13)	C11—C6—C7—F1	-178.12 (12)
N1—N2—N3—N4	-0.81 (18)	N1—C6—C7—F1	1.09 (18)
N2—N3—N4—C5	0.94 (19)	C11—C6—C7—C8	0.5 (2)
N3—N4—C5—N1	-0.62 (16)	N1—C6—C7—C8	179.75 (13)
N3—N4—C5—S1	179.93 (11)	F1—C7—C8—C9	177.56 (13)
N2—N1—C5—N4	0.11 (15)	C6—C7—C8—C9	-1.1 (2)
C6—N1—C5—N4	175.73 (13)	C7—C8—C9—C10	0.7 (2)
N2—N1—C5—S1	179.57 (11)	C8—C9—C10—C11	0.3 (2)
C6—N1—C5—S1	-4.8 (2)	C9—C10—C11—C6	-0.9 (2)
C5—N1—C6—C7	-116.67 (15)	C7—C6—C11—C10	0.4 (2)
N2—N1—C6—C7	58.59 (18)	N1—C6—C11—C10	-178.76 (12)
C5—N1—C6—C11	62.53 (19)		

Hydrogen-bond geometry (Å, °)

<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>
N4—H4 \cdots S1 ⁱ	0.90 (2)	2.35 (2)	3.2456 (12)	173.2 (18)

C5—S1 \cdots Cg1 ⁱⁱ	1.67 (1)	3.77 (1)	4.0760 (14)	88 (1)
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Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, y, -z+1/2$.