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1*H*-Pyrazolo[4,3-*g*]benzothiazol-7-amineJosé R. Camacho^{a*} and Teresa González^{b*}

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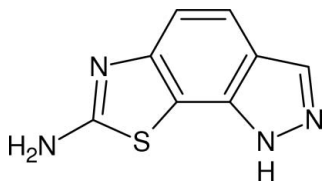
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.117; data-to-parameter ratio = 13.3.

The molecule of the title compound, $\text{C}_8\text{H}_6\text{N}_4\text{S}$, is almost planar [maximum deviation from the mean plane = 0.020 (1) Å for the S atom]. In the crystal, a supramolecular three-dimensional arrangement arises from $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds and weak aromatic stacking interactions along the a axis [centroid-centroid separation = 3.582 (2) Å].

Related literature

For background on DNA intercalation agents, see: Cagnoli *et al.* (1968); Martínez & Chacón-García (2005); Chakrabarty *et al.* (2008). For further synthetic details, see: Salazar & Dorta (2004).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{N}_4\text{S}$
 $M_r = 190.23$
 Monoclinic, $P2_1/c$
 $a = 4.499$ (2) Å
 $b = 14.979$ (8) Å
 $c = 12.112$ (7) Å
 $\beta = 92.442$ (19)°

$V = 815.6$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.35$ mm⁻¹
 $T = 293$ K
 $0.50 \times 0.48 \times 0.28$ mm

Data collection

Rigaku AFC7S Mercury diffractometer
 Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.837$, $T_{\max} = 0.904$

8415 measured reflections
 1564 independent reflections
 1356 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.117$
 $S = 1.12$
 1564 reflections

118 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{N3}^{\text{i}}$	0.95	1.92	2.864 (3)	170
$\text{N4}-\text{H5}\cdots\text{N1}^{\text{ii}}$	0.98	2.19	3.123 (3)	158
$\text{N4}-\text{H6}\cdots\text{N1}^{\text{iii}}$	0.95	2.09	3.019 (3)	164

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2931).

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supplementary materials

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Comment

Most of the significant advances against diseases have been made by designing and testing new structures, which are often heteroaromatic derivatives. Actually, the discovery of new compounds with antitumoral activity has become one of the most important goals in medicinal chemistry. One interesting group of potential chemotherapeutic agents includes molecules which interact with DNA like intercalator agents (Martínez & Chacón-García, 2005). Intercalation occurs when ligands of an appropriate size and chemical nature, fit themselves in between base pairs of DNA. Such ligands are mostly polycyclic, aromatic and planar. These kinds of agents are used in chemotherapeutic treatment to inhibit DNA replication in rapidly growing cancer cells. The title compound (I) is a polycyclic, aromatic and heterocyclic molecule and could be used to develop a new type of DNA intercalators agents (Chakrabarty *et al.* 2008).

The molecular structure is shown in figure 1, with its respective labels. The molecule adopts a conformation essentially planar, with maximum deviation of the mean plane of 0.020 (1) Å for atom S1. The crystal structure of (I), consists of the self-assembly of the molecules through hydrogen bonding interactions of the kind N—H...N. The crystal packing (Fig. 2), consists of infinite chains in zigzag along the *b* axis generated by intermolecular interactions of hydrogen bond between the amino group and N atom of the imidazole ring [N1...N4 = 3.019 (3) Å]. These chains are connected through the interaction between the atoms N2 and N3 forming a two-dimensional wavy-like arrangement in the *bc* plane. These layers are stacking through weak π - π interactions along the *a* axis (Cg3...Cg1, where Cg3 = C2/C3/C4/C5/C7/C8 and Cg1 = S1/C6/N3/C5/C7) together with an additional hydrogen bond lead to the formation of a three-dimensional hydrogen bonded network.

Experimental

To a solution of 6-aminoindazole (2.00 g, 15 mmol) and NH₄SCN (2.29 g, 30 mmol) in acetic acid (25 ml) was added dropwise pentylpyridinium tribromide (5.86 g, 15 mmol) (Salazar & Dorta, 2004). The resulting solution was stirred for 3 h at room temperature and then, 3 h at 80°C. The reaction mixture was then poured into ice (50 g), the precipitate was filtered and discarded. The resulting solution was neutralized with K₂CO₃, and the formed precipitate was filtered, washed with AcOEt and dried; to give a yellow powder corresponding to the title compound. Yield: 1.80 g (63%). The melting point (uncorrected) was measured with a Fischer-Johns micro hot-stage apparatus: d 563 K.

The yellow powder was dissolved in a minimum amount of 1,4-dioxane and the solution was left for several days at room temperature, during which the solution gradually reduced its volume to give light brown blocks of (I).

IR data [KBr pellets, (cm⁻¹): 3367, 3314, 3181, 1629. ¹H NMR [500 MHz, DMSO-d₆, d (p.p.m.)]: 13.04 (brs, 1H, NH), 8.05 (s, 1H), 7.57 (d, 1H, J = 6.84 Hz), 7.45 (brs, 2H, NH₂), 7.21 (d, 1H, J = 6.88 Hz). ¹³C NMR [126 MHz, DMSO-d₆, d (p.p.m.)]: 166.97 (C6), 152.21 (C5), 135.41 (C1), 134.99 (C2), 119.13 (C8), 118.01 (C3), 113.95 (C4), 109.39 (C7).

Refinement

The N-bound H atoms were located in difference maps and refined as riding in their as found relative positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The C-bound H atoms were placed in idealized positions (C—H = 0.93–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

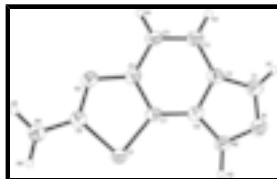


Fig. 1. The molecular structure of (I), showing displacement ellipsoids drawn at the 35% probability level and H atoms shown as spheres of arbitrary radius.

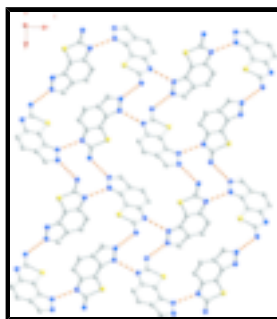


Fig. 2. View of the hydrogen bonded layer in the *bc* plane in (I). The H atoms have been omitted for clarity and dashed lines indicate the donor...acceptor interactions for hydrogen bonds.

(I)

Crystal data

$\text{C}_8\text{H}_6\text{N}_4\text{S}$

$M_r = 190.23$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 4.499\ (2)\ \text{\AA}$

$b = 14.979\ (8)\ \text{\AA}$

$c = 12.112\ (7)\ \text{\AA}$

$\beta = 92.442\ (19)^\circ$

$V = 815.6\ (7)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 392$

$D_x = 1.549\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71070\ \text{\AA}$

Cell parameters from 5546 reflections

$\theta = 1.4\text{--}27.8^\circ$

$\mu = 0.35\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, light brown

$0.50 \times 0.48 \times 0.28\ \text{mm}$

Data collection

Rigaku AFC7S Mercury
diffractometer

Radiation source: Normal-focus sealed tube

Monochromator: graphite

1564 independent reflections

1356 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$T = 293$ K $\theta_{\max} = 27.8^\circ$
 ω scans $\theta_{\min} = 2.2^\circ$
 Absorption correction: Multi-scan
 (Jacobson, 1998) $h = -5 \rightarrow 5$
 $T_{\min} = 0.837$, $T_{\max} = 0.904$ $k = -17 \rightarrow 17$
 8415 measured reflections $l = -10 \rightarrow 13$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.043$ H-atom parameters constrained
 $wR(F^2) = 0.117$ $w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.4259P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.12$ $(\Delta/\sigma)_{\max} = 0.001$
 1564 reflections $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 118 parameters $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$
 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.01959 (12)	0.29819 (4)	0.80928 (4)	0.0375 (2)
N1	0.4558 (5)	0.03847 (13)	0.69844 (15)	0.0469 (5)
N2	0.6362 (4)	0.11194 (12)	0.70868 (14)	0.0399 (5)
H2	0.7275	0.1305	0.6432	0.048*
N3	0.8801 (4)	0.31237 (12)	1.01512 (15)	0.0374 (4)
N4	1.2153 (5)	0.42105 (13)	0.95801 (16)	0.0467 (5)
H6	1.3202	0.4479	0.8999	0.056*
H5	1.2408	0.4424	1.0345	0.056*
C1	0.3414 (6)	0.02732 (16)	0.79596 (19)	0.0447 (6)
H1	0.2103	-0.0183	0.8125	0.054*
C2	0.4424 (5)	0.09335 (14)	0.87253 (17)	0.0364 (5)
C3	0.3893 (5)	0.11384 (15)	0.98363 (18)	0.0425 (5)

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H3	0.2600	0.0790	1.0233	0.051*
C4	0.5305 (5)	0.18567 (15)	1.03243 (18)	0.0408 (5)
H4	0.4976	0.1996	1.1057	0.049*
C5	0.7267 (5)	0.23892 (14)	0.97160 (16)	0.0352 (5)
C6	1.0420 (5)	0.34903 (14)	0.94037 (17)	0.0354 (5)
C7	0.7767 (5)	0.22046 (13)	0.86132 (16)	0.0319 (5)
C8	0.6336 (5)	0.14676 (14)	0.81177 (16)	0.0333 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0429 (4)	0.0374 (4)	0.0325 (4)	-0.0007 (2)	0.0051 (2)	0.00195 (19)
N1	0.0621 (14)	0.0372 (11)	0.0414 (11)	-0.0055 (9)	0.0022 (9)	-0.0022 (8)
N2	0.0526 (12)	0.0365 (10)	0.0308 (10)	-0.0003 (9)	0.0058 (8)	-0.0021 (7)
N3	0.0424 (11)	0.0372 (10)	0.0326 (10)	0.0027 (8)	0.0028 (8)	-0.0032 (7)
N4	0.0574 (13)	0.0421 (11)	0.0405 (11)	-0.0088 (9)	0.0014 (9)	0.0000 (8)
C1	0.0550 (15)	0.0365 (12)	0.0426 (13)	-0.0047 (10)	0.0028 (10)	0.0023 (9)
C2	0.0414 (13)	0.0312 (11)	0.0367 (11)	0.0028 (9)	0.0031 (9)	0.0043 (8)
C3	0.0489 (14)	0.0417 (13)	0.0375 (12)	-0.0020 (10)	0.0084 (10)	0.0051 (9)
C4	0.0503 (14)	0.0439 (13)	0.0290 (11)	0.0011 (10)	0.0091 (10)	0.0018 (8)
C5	0.0385 (12)	0.0340 (11)	0.0331 (11)	0.0060 (9)	0.0029 (8)	0.0005 (8)
C6	0.0363 (12)	0.0334 (11)	0.0364 (11)	0.0055 (9)	-0.0002 (8)	0.0019 (8)
C7	0.0346 (12)	0.0323 (11)	0.0289 (10)	0.0054 (9)	0.0038 (8)	0.0016 (8)
C8	0.0384 (12)	0.0312 (11)	0.0303 (10)	0.0083 (9)	0.0011 (8)	0.0007 (8)

Geometric parameters (\AA , $^\circ$)

S1—C7	1.734 (2)	C1—C2	1.418 (3)
S1—C6	1.760 (2)	C1—H1	0.9300
N1—C1	1.319 (3)	C2—C8	1.405 (3)
N1—N2	1.370 (3)	C2—C3	1.411 (3)
N2—C8	1.354 (3)	C3—C4	1.371 (3)
N2—H2	0.9500	C3—H3	0.9300
N3—C6	1.307 (3)	C4—C5	1.419 (3)
N3—C5	1.391 (3)	C4—H4	0.9300
N4—C6	1.343 (3)	C5—C7	1.392 (3)
N4—H6	0.9529	C7—C8	1.400 (3)
N4—H5	0.9822		
C7—S1—C6	88.59 (10)	C2—C3—H3	120.4
C1—N1—N2	105.85 (18)	C3—C4—C5	120.3 (2)
C8—N2—N1	111.39 (18)	C3—C4—H4	119.9
C8—N2—H2	132.7	C5—C4—H4	119.9
N1—N2—H2	115.8	N3—C5—C7	115.03 (19)
C6—N3—C5	110.62 (18)	N3—C5—C4	123.89 (19)
C6—N4—H6	121.6	C7—C5—C4	121.1 (2)
C6—N4—H5	117.1	N3—C6—N4	124.3 (2)
H6—N4—H5	121.2	N3—C6—S1	115.53 (17)
N1—C1—C2	111.8 (2)	N4—C6—S1	120.12 (16)

N1—C1—H1	124.1	C5—C7—C8	118.54 (19)
C2—C1—H1	124.1	C5—C7—S1	110.22 (16)
C8—C2—C3	120.5 (2)	C8—C7—S1	131.23 (16)
C8—C2—C1	103.94 (19)	N2—C8—C7	132.6 (2)
C3—C2—C1	135.5 (2)	N2—C8—C2	107.05 (19)
C4—C3—C2	119.2 (2)	C7—C8—C2	120.32 (19)
C4—C3—H3	120.4		

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>
N2—H2 \cdots N3 ⁱ	0.95	1.92	2.864 (3)	170
N4—H5 \cdots N1 ⁱⁱ	0.98	2.19	3.123 (3)	158
N4—H6 \cdots N1 ⁱⁱⁱ	0.95	2.09	3.019 (3)	164

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $x+1, -y+1/2, z+1/2$; (iii) $-x+2, y+1/2, -z+3/2$.

Fig. 1

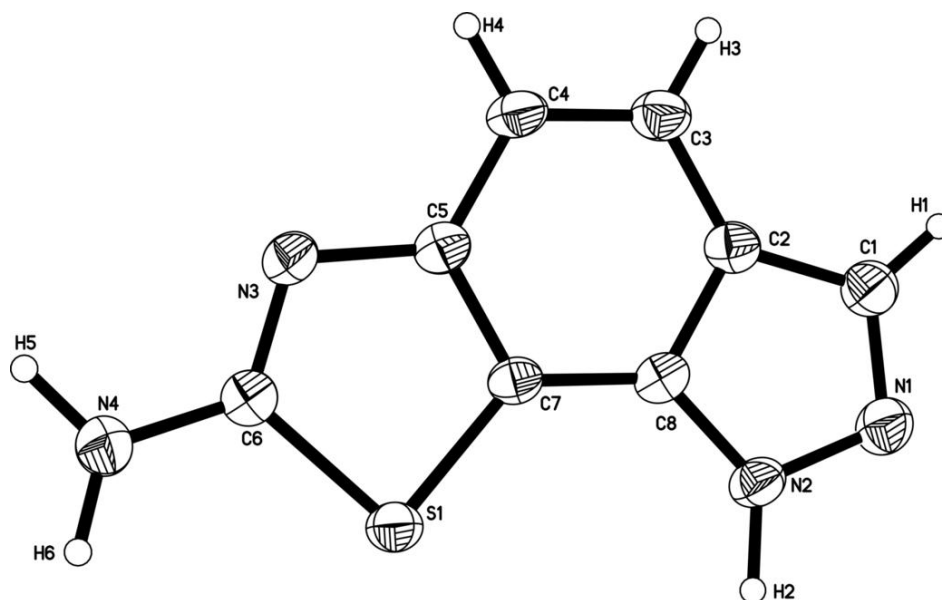


Fig. 2

