

rac-3-(5-Amino-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-phenylthiazolidin-4-one: sheets built from N—H···N and C—H··· π (arene) hydrogen bonds

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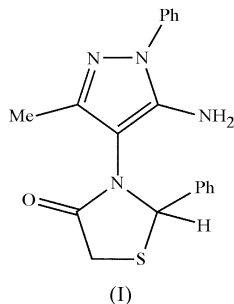
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The title compound, C₁₉H₁₈N₄OS, crystallizes in space group $P\bar{1}$ with $Z' = 2$. The two molecules in the selected asymmetric unit are nearly enantiomorphous. The molecules are linked by two N—H···N hydrogen bonds [H···N both 2.20 Å, N···N = 3.064 (3) and 3.077 (3) Å, and N—H···N = 165 and 172°] into C₂²(10) chains, and these chains are linked into sheets by two independent C—H··· π (arene) hydrogen bonds.

Comment

The three-component cyclocondensation reaction between 4,5-diamino-3-methyl-1-phenyl-1*H*-pyrazole, benzaldehyde and 2-mercaptoacetic acid provides the title compound, (I), rather than the expected pyrazolodiazepine (Low *et al.*, 2003).



Compound (I) crystallizes in the centrosymmetric space group $P\bar{1}$, with $Z' = 2$. The asymmetric unit was selected to provide the simplest description of the N—H···N hydrogen bonds and in these circumstances the two independent molecules (Fig. 1) are of opposite configuration. Molecule 1, containing atom S11, has the *S* configuration at the stereogenic centre C12, while molecule 2, containing atom S21, has the *R*

configuration at C22. The space group accommodates equal numbers of both configurations of both molecules. The two independent molecules are themselves close to being enantiomers, as shown qualitatively by Fig. 1 and quantitatively by the key torsion angles (Table 1). Atoms N13 and N23 are both effectively planar, while atoms N15 and N25 are both markedly pyramidal. In each molecule, the two S—C distances show distinctly different values (Table 1), but all of the other distances are typical of their types (Allen *et al.*, 1987).

The molecules of (I) are linked into sheets by a combination of N—H···N and C—H··· π (arene) hydrogen bonds (Table 2). Within the selected asymmetric unit, amino atom N15 acts as hydrogen-bond donor, *via* atom H15A, to ring atom N22.

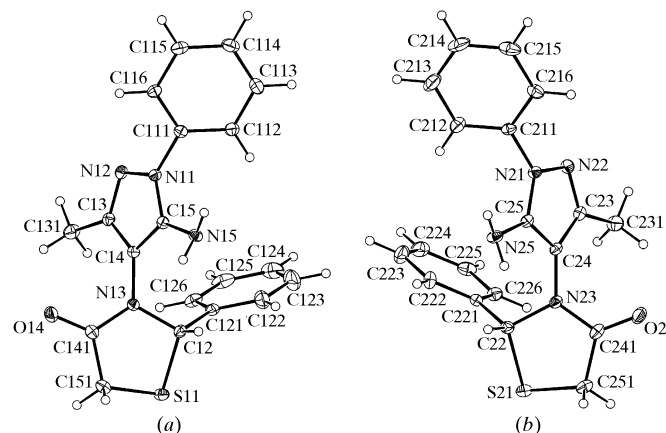


Figure 1
The two independent molecules, *viz.* (a) the *S* enantiomer and (b) the *R* enantiomer, in the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

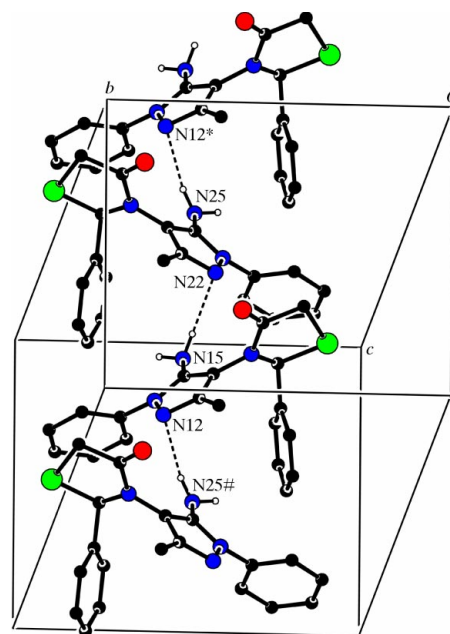


Figure 2
Part of the crystal structure of (I), showing the formation of a C₂²(10) chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x - 1, y, z$) and ($1 + x, y, z$), respectively.

Similarly, amino atom N25 in the type 2 molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H25A, to ring atom N12 in the type 1 molecule at $(x - 1, y, z)$, so generating by translation a $C_2^2(10)$ chain (Bernstein *et al.*, 1995) running parallel to the $[100]$ direction (Fig. 2). This chain lies wholly in the domain $-0.03 < z < 0.51$, and a second antiparallel chain, related to the first by inversion, lies in the domain $0.49 < z < 1.03$.

Within each domain, the $[100]$ chains are linked by a pair of $C-H \cdots \pi(\text{arene})$ hydrogen bonds. Atom C115 in the type 1 molecule at (x, y, z) acts as hydrogen-bond donor to ring C121–C126 in the type 1 molecule at $(x, 1 + y, z)$, so forming by translation a chain running parallel to the $[010]$ direction (Fig. 3a). In an entirely similar manner, atom C215 in the type 2 molecule at (x, y, z) acts as donor to ring C221–C226 in the

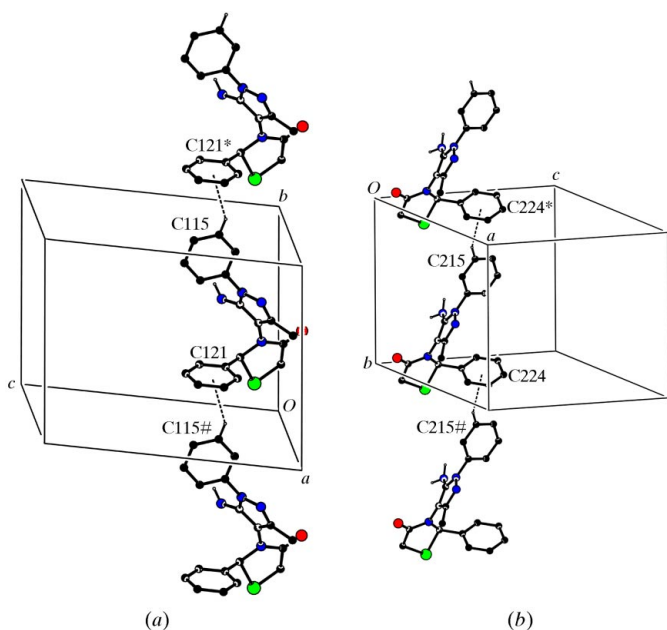


Figure 3 Part of the crystal structure of (I), showing the formation of the $C-H \cdots \pi(\text{arene})$ chains along $[010]$. (a) A chain formed by the type 1 molecules; atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, y - 1, z)$, respectively. (b) A chain formed by the type 2 molecules; atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y - 1, z)$ and $(x, 1 + y, z)$, respectively. For the sake of clarity, H atoms bonded to C atoms and not involved in the motif shown have been omitted.

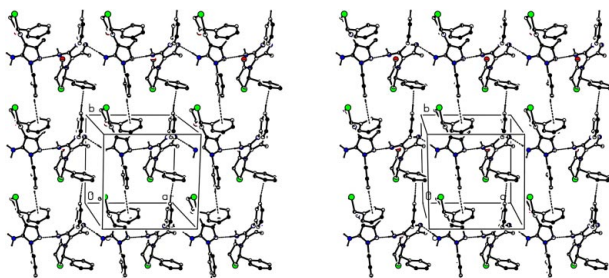


Figure 4 A stereoview of part of the crystal structure of (I), showing the formation of an (001) sheet by the combination of the $[100]$ and $[010]$ chains. For the sake of clarity, H atoms bonded to C atoms and not involved in the motif shown have been omitted.

type 2 molecule at $(x, y - 1, z)$ (Fig. 3b). These two independent $[010]$ chains thus link all of the $[100]$ chains within a given domain of z into an (001) sheet (Fig. 4). Two sheets, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent sheets. It is notable that each of the amino groups acts only as a single donor of hydrogen bonds; there are no other potential acceptors within suitable hydrogen-bonding distance of either N15 or N25.

Experimental

For the preparation of (I), a solution of 4,5-diamino-3-methyl-1-phenyl-1H-pyrazole (1.0 mmol), benzaldehyde (1.0 mmol) and 2-mercaptoacetic acid (2.0 mmol) in anhydrous benzene (10 ml) was heated under reflux for 17 h; the progress of the reaction was monitored by thin-layer chromatography. When the reaction was complete, the mixture was cooled and the solvent was evaporated. The resulting solid residue was recrystallized from dimethylformamide giving crystals of (I) suitable for single-crystal X-ray diffraction (m.p. 437 K, yield 65%). MS (EI, 70 eV) m/z (%): 350 (M^+ , 100), 245 (80), 200 (44), 173 (32), 135 (49), 119 (39), 91 (23), 77 (70), 51 (19), 46 (15).

Crystal data

$C_{19}H_{18}N_4OS$
 $M_r = 350.44$
 Triclinic, $P\bar{1}$
 $a = 10.7937$ (4) Å
 $b = 11.3989$ (2) Å
 $c = 14.2448$ (5) Å
 $\alpha = 79.993$ (2)°
 $\beta = 83.3490$ (14)°
 $\gamma = 89.852$ (2)°
 $V = 1714.07$ (9) Å³

$Z = 4$
 $D_x = 1.358$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 7923 reflections
 $\theta = 2.9$ – 27.6 °
 $\mu = 0.20$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.18 \times 0.10 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.945$, $T_{\max} = 0.990$
 7923 measured reflections

7923 independent reflections
 5732 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.154$
 $\theta_{\text{max}} = 27.6$ °
 $h = -14 \rightarrow 14$
 $k = -14 \rightarrow 14$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.184$
 $S = 1.03$
 7923 reflections
 453 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 0.9869P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.63$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S11–C12	1.830 (2)	S21–C22	1.828 (2)
S11–C151	1.796 (3)	S21–C251	1.795 (3)
C12–N13–C141	117.5 (2)	C22–N23–C241	117.5 (2)
C12–N13–C14	119.13 (19)	C22–N23–C24	118.13 (19)
C14–N13–C141	122.9 (2)	C24–N23–C241	124.1 (2)
C13–C14–N13–C12	121.7 (3)	C23–C24–N23–C22	−117.7 (3)
N12–N11–C111–C112	−115.9 (3)	N22–N21–C211–C212	109.5 (3)
N13–C12–C121–C122	131.5 (3)	N23–C22–C221–C222	−119.1 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

Cg1 is the centroid of ring C161–C166 and Cg2 is the centroid of ring C261–C266.

<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>
N15–H15A···N22	0.88	2.20	3.077 (3)	172
N25–H25A···N12 ⁱ	0.88	2.20	3.064 (3)	165
C125–H125···Cg1 ⁱⁱ	0.95	2.88	3.691 (3)	144
C225–H225···Cg2 ⁱⁱⁱ	0.95	2.93	3.794 (4)	152

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

Crystals of compound (I) are triclinic and space group $P\bar{1}$ was selected and confirmed by the structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with distances C–H = 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH) and N–H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1731). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Low, J. N., Insuasty, B., Mosquera, M. & Cobo, J. (2003). *Acta Cryst.* **E59**, o614–o615.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre Chemistry Department, NUI Galway, Ireland.
- Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.