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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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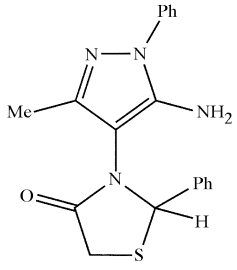
The title compound, $C_{19}H_{18}N_4OS$, crystallizes in space group $P\overline{1}$ with $Z' = 2$. The two molecules in the selected asymmetric unit are nearly enantiomorphous. The molecules are linked by two N—H···N hydrogen bonds [H···N both 2.20 Å, N···N = 3.064 (3) and 3.077 (3) Å, and N—H···N = 165 and 172°] into $C_2^2(10)$ 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).



(I)

Compound (I) crystallizes in the centrosymmetric space group $P\overline{1}$, 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 H15*A*, to ring atom N22.

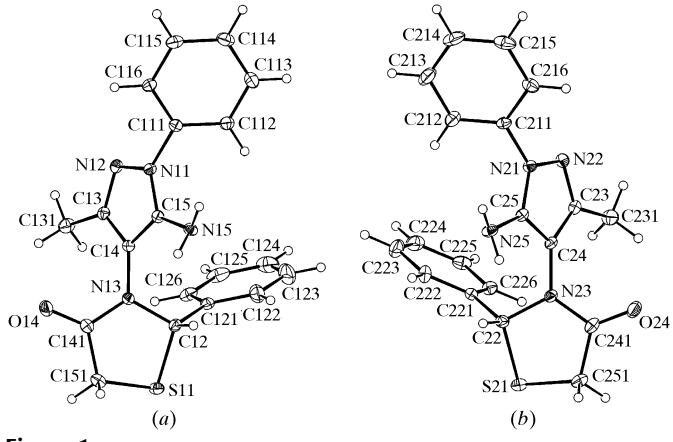


Figure 1
The two independent molecules, *viz*. (*a*) the *S* enantiomer and (*b*) the *R* enantiomer, in the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

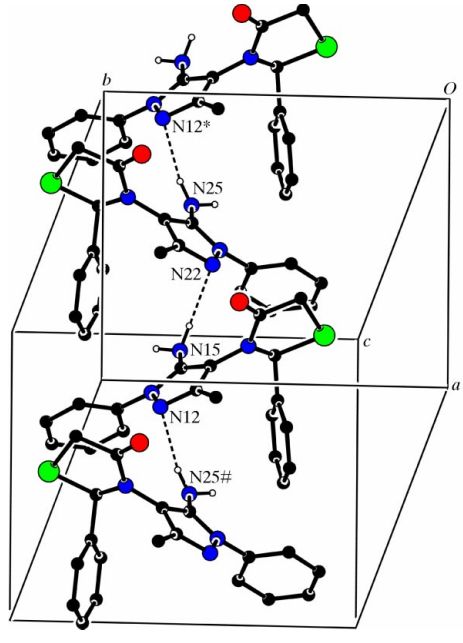


Figure 2
Part of the crystal structure of (I), showing the formation of a $C_2^2(10)$ chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x - 1, y, z)$ and $(1 + x, y, z)$, respectively.

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Similarly, amino atom N25 in the type 2 molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H25*A*, 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···π(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. 3*a*). 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 type 2 molecule at $(x, y-1, z)$ (Fig. 3*b*). 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.

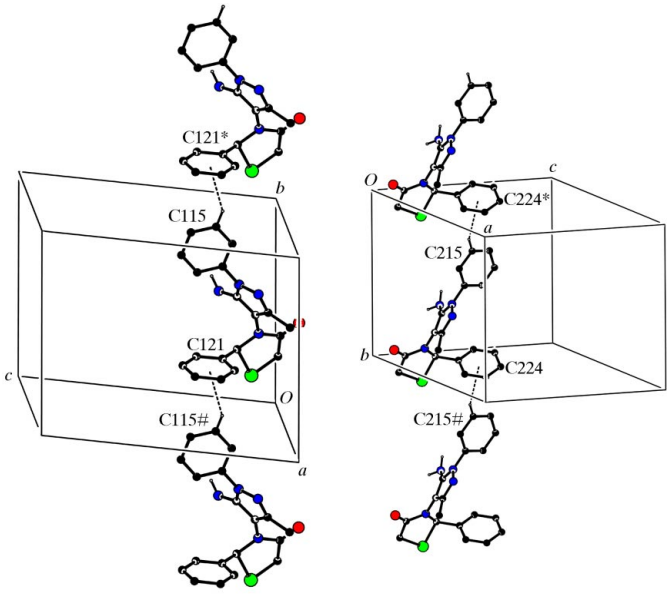

Figure 3
Part of the crystal structure of (I), showing the formation of the C—H···π(arene) chains along [010]. (*a*) A chain formed by the type 1 molecules; atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, 1+y, z)$ and $(x, y-1, z)$, respectively. (*b*) A chain formed 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.

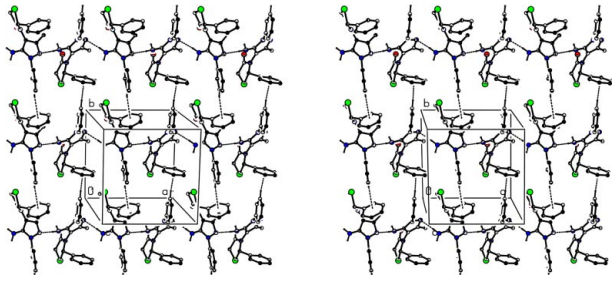

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of an (001) sheet by the combination of the [100] and [010] chains. For the sake of clarity, H atoms bonded to C atoms and not involved in the motif shown have been omitted.

Experimental

For the preparation of (I), a solution of 4,5-diamino-3-methyl-1-phenyl-1*H*-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, $P\overline{1}$
$a = 10.7937$ (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) Å^3
$Z = 4$
$D_x = 1.358$ 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 × 0.10 × 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 $I > 2\sigma(I)$
$R_{int} = 0.154$
$\theta_{max} = 27.6$°
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ 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, °).

*Cg*1 is the centroid of ring C161–C166 and *Cg*2 is the centroid of ring C261–C266.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N15—H15*A*···N22	0.88	2.20	3.077 (3)	172
N25—H25*A*···N12^{i}	0.88	2.20	3.064 (3)	165
C125—H125···*Cg*1^{ii}	0.95	2.88	3.691 (3)	144
C225—H225···*Cg*2^{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 $P\overline{1}$ 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 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic CH) and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(C_{methyl})$.

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 *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JC thanks the Consejería de Educación y Ciencia (Junta de Andalucía, Spain) and the Universidad de Jaen for financial support. BI and FO thank COLCIENCIAS and the Universidad de Valle for financial support.

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.

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supporting information

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rac-3-(5-Amino-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-phenyl-thiazolidin-4-one

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Hall symbol: -P 1
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$b = 11.3989\ (2)$ Å
$c = 14.2448\ (5)$ Å
$\alpha = 79.993\ (2)°$
$\beta = 83.3490\ (14)°$
$\gamma = 89.852\ (2)°$
$V = 1714.07\ (9)$ Å^3
$Z = 4$
$F(000) = 736$
$D_x = 1.358$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7923 reflections
$\theta = 2.9–27.6°$
$\mu = 0.20$ mm^{-1}
$T = 120$ K
Plate, colourless
0.18 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: rotating anode
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.154$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.9°$
$h = -14\rightarrow14$
$k = -14\rightarrow14$
$l = -18\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.184$
$S = 1.03$
7923 reflections
453 parameters
0 restraints
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

$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 0.9869P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N11	0.85511 (18)	0.79824 (17)	0.22013 (14)	0.0185 (4)
C111	0.8604 (2)	0.8800 (2)	0.28480 (17)	0.0196 (5)
C112	0.8536 (3)	0.8364 (2)	0.38289 (19)	0.0275 (6)
C113	0.8631 (3)	0.9152 (3)	0.4453 (2)	0.0347 (7)
C114	0.8805 (3)	1.0359 (3)	0.4102 (2)	0.0337 (7)
C115	0.8866 (3)	1.0781 (2)	0.3125 (2)	0.0305 (6)
C116	0.8757 (2)	1.0001 (2)	0.24911 (19)	0.0228 (5)
N12	0.95853 (18)	0.78939 (18)	0.15424 (14)	0.0198 (4)
C13	0.9313 (2)	0.6970 (2)	0.11393 (17)	0.0196 (5)
C131	1.0205 (3)	0.6601 (3)	0.0366 (2)	0.0302 (6)
C14	0.8142 (2)	0.6467 (2)	0.15270 (17)	0.0171 (5)
S11	0.69650 (6)	0.31661 (6)	0.15698 (5)	0.02537 (17)
C12	0.7213 (2)	0.4446 (2)	0.21477 (17)	0.0204 (5)
C121	0.8213 (2)	0.4181 (2)	0.28088 (18)	0.0230 (5)
C122	0.7904 (3)	0.4077 (3)	0.3795 (2)	0.0393 (7)
C123	0.8823 (4)	0.3820 (3)	0.4408 (3)	0.0567 (10)
C124	1.0028 (4)	0.3672 (3)	0.4042 (3)	0.0551 (11)
C125	1.0342 (3)	0.3755 (3)	0.3057 (3)	0.0430 (8)
C126	0.9437 (3)	0.4011 (2)	0.2449 (2)	0.0310 (6)
N13	0.75797 (19)	0.54165 (18)	0.13443 (14)	0.0190 (4)
C141	0.7223 (2)	0.5319 (2)	0.04727 (18)	0.0224 (5)
O14	0.73897 (19)	0.60938 (17)	−0.02410 (13)	0.0311 (4)
C151	0.6592 (3)	0.4129 (2)	0.05056 (19)	0.0260 (6)
C15	0.7672 (2)	0.7136 (2)	0.22053 (17)	0.0185 (5)
N15	0.65687 (19)	0.70138 (19)	0.28103 (14)	0.0214 (4)
N21	0.35762 (19)	0.60474 (18)	0.21808 (14)	0.0195 (4)
C211	0.3629 (2)	0.4962 (2)	0.28478 (18)	0.0211 (5)
C212	0.3645 (3)	0.5013 (3)	0.38099 (19)	0.0307 (6)
C213	0.3727 (3)	0.3963 (3)	0.4460 (2)	0.0431 (8)
C214	0.3814 (3)	0.2894 (3)	0.4132 (2)	0.0443 (8)
C215	0.3808 (3)	0.2851 (3)	0.3175 (2)	0.0403 (8)
C216	0.3710 (3)	0.3895 (2)	0.2517 (2)	0.0284 (6)
N22	0.46191 (19)	0.64247 (18)	0.15401 (14)	0.0209 (4)
C23	0.4336 (2)	0.7510 (2)	0.11225 (17)	0.0207 (5)
C231	0.5229 (3)	0.8226 (3)	0.0369 (2)	0.0319 (6)
C24	0.3137 (2)	0.7832 (2)	0.14798 (17)	0.0183 (5)
S21	0.19369 (6)	1.11124 (6)	0.15142 (5)	0.02540 (18)
C22	0.2224 (2)	0.9589 (2)	0.20869 (17)	0.0209 (5)
C221	0.3273 (2)	0.9564 (2)	0.27099 (17)	0.0207 (5)
C222	0.3079 (3)	0.9035 (3)	0.36676 (18)	0.0303 (6)
C223	0.4051 (3)	0.9002 (3)	0.4239 (2)	0.0401 (8)

C224	0.5200 (3)	0.9498 (3)	0.3846 (2)	0.0367 (7)
C225	0.5400 (3)	1.0021 (2)	0.2887 (2)	0.0298 (6)
C226	0.4437 (2)	1.0053 (2)	0.23233 (19)	0.0254 (6)
N23	0.25669 (19)	0.89500 (17)	0.12829 (14)	0.0203 (4)
C241	0.2220 (2)	0.9432 (2)	0.04141 (18)	0.0252 (6)
O24	0.2395 (2)	0.89702 (17)	−0.03008 (13)	0.0334 (5)
C251	0.1597 (3)	1.0617 (2)	0.04410 (19)	0.0277 (6)
C25	0.2672 (2)	0.6865 (2)	0.21657 (17)	0.0187 (5)
N25	0.15642 (19)	0.67233 (19)	0.27590 (15)	0.0238 (5)
H112	0.8427	0.7534	0.4066	0.033*
H113	0.8576	0.8865	0.5124	0.042*
H114	0.8883	1.0898	0.4532	0.040*
H115	0.8984	1.1610	0.2887	0.037*
H116	0.8786	1.0289	0.1822	0.027*
H13A	1.0937	0.7136	0.0234	0.045*
H13B	0.9796	0.6642	−0.0218	0.045*
H13C	1.0467	0.5782	0.0575	0.045*
H12	0.6417	0.4643	0.2517	0.025*
H122	0.7067	0.4181	0.4051	0.047*
H123	0.8611	0.3749	0.5082	0.068*
H124	1.0654	0.3511	0.4461	0.066*
H125	1.1178	0.3637	0.2805	0.052*
H126	0.9653	0.4071	0.1776	0.037*
H15C	0.6898	0.3790	−0.0071	0.031*
H15D	0.5678	0.4222	0.0526	0.031*
H15A	0.5958	0.6828	0.2501	0.026*
H15B	0.6302	0.7632	0.3064	0.026*
H212	0.3600	0.5758	0.4024	0.037*
H213	0.3724	0.3982	0.5124	0.052*
H214	0.3879	0.2177	0.4575	0.053*
H215	0.3870	0.2106	0.2962	0.048*
H216	0.3700	0.3871	0.1855	0.034*
H23A	0.5959	0.7747	0.0225	0.048*
H23B	0.5493	0.8938	0.0598	0.048*
H23C	0.4823	0.8466	−0.0214	0.048*
H22	0.1447	0.9228	0.2481	0.025*
H222	0.2287	0.8694	0.3936	0.036*
H223	0.3921	0.8638	0.4896	0.048*
H224	0.5858	0.9481	0.4236	0.044*
H225	0.6195	1.0355	0.2618	0.036*
H226	0.4572	1.0413	0.1666	0.030*
H25C	0.0684	1.0527	0.0445	0.033*
H25D	0.1921	1.1204	−0.0131	0.033*
H25A	0.0959	0.7129	0.2498	0.029*
H25B	0.1307	0.5991	0.3005	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0176 (10)	0.0172 (10)	0.0205 (10)	−0.0003 (8)	−0.0005 (8)	−0.0039 (8)
C111	0.0149 (12)	0.0223 (12)	0.0225 (12)	0.0007 (9)	−0.0035 (9)	−0.0056 (10)
C112	0.0318 (15)	0.0236 (13)	0.0274 (14)	−0.0046 (11)	−0.0087 (11)	−0.0017 (11)
C113	0.0401 (17)	0.0415 (17)	0.0236 (14)	−0.0068 (13)	−0.0041 (12)	−0.0085 (12)
C114	0.0332 (16)	0.0344 (16)	0.0370 (16)	−0.0059 (13)	−0.0003 (13)	−0.0180 (13)
C115	0.0300 (15)	0.0218 (14)	0.0399 (16)	−0.0046 (11)	−0.0005 (12)	−0.0079 (12)
C116	0.0195 (13)	0.0216 (13)	0.0264 (13)	−0.0019 (10)	−0.0005 (10)	−0.0032 (10)
N12	0.0164 (10)	0.0220 (11)	0.0200 (10)	0.0007 (8)	0.0003 (8)	−0.0023 (8)
C13	0.0208 (12)	0.0176 (12)	0.0197 (12)	0.0032 (9)	−0.0023 (10)	−0.0016 (9)
C131	0.0266 (14)	0.0278 (14)	0.0348 (15)	−0.0023 (11)	0.0078 (12)	−0.0093 (12)
C14	0.0162 (11)	0.0161 (11)	0.0195 (11)	0.0016 (9)	−0.0043 (9)	−0.0031 (9)
S11	0.0275 (4)	0.0201 (3)	0.0296 (4)	−0.0031 (3)	−0.0046 (3)	−0.0065 (3)
C12	0.0208 (12)	0.0190 (12)	0.0204 (12)	−0.0007 (10)	0.0011 (10)	−0.0025 (9)
C121	0.0289 (14)	0.0156 (12)	0.0249 (13)	−0.0014 (10)	−0.0056 (11)	−0.0026 (10)
C122	0.055 (2)	0.0350 (17)	0.0283 (15)	0.0055 (14)	−0.0086 (14)	−0.0050 (12)
C123	0.085 (3)	0.052 (2)	0.0357 (18)	0.002 (2)	−0.029 (2)	−0.0012 (16)
C124	0.070 (3)	0.0323 (18)	0.068 (3)	−0.0026 (17)	−0.050 (2)	0.0030 (16)
C125	0.0321 (17)	0.0238 (15)	0.073 (2)	−0.0030 (12)	−0.0221 (16)	0.0022 (15)
C126	0.0293 (15)	0.0206 (13)	0.0419 (16)	−0.0032 (11)	−0.0067 (12)	0.0001 (11)
N13	0.0217 (11)	0.0180 (10)	0.0178 (10)	0.0003 (8)	−0.0023 (8)	−0.0041 (8)
C141	0.0214 (13)	0.0246 (13)	0.0222 (13)	0.0036 (10)	−0.0034 (10)	−0.0063 (10)
O14	0.0417 (12)	0.0292 (10)	0.0228 (9)	0.0017 (9)	−0.0083 (8)	−0.0033 (8)
C151	0.0251 (14)	0.0289 (14)	0.0269 (13)	0.0005 (11)	−0.0067 (11)	−0.0104 (11)
C15	0.0155 (11)	0.0209 (12)	0.0191 (11)	0.0007 (9)	−0.0043 (9)	−0.0023 (9)
N15	0.0190 (11)	0.0240 (11)	0.0227 (10)	−0.0004 (8)	−0.0005 (8)	−0.0092 (8)
N21	0.0168 (10)	0.0188 (10)	0.0211 (10)	0.0010 (8)	−0.0006 (8)	0.0005 (8)
C211	0.0177 (12)	0.0180 (12)	0.0253 (13)	0.0004 (9)	−0.0016 (10)	0.0016 (10)
C212	0.0356 (16)	0.0287 (15)	0.0263 (14)	0.0005 (12)	−0.0065 (12)	0.0013 (11)
C213	0.049 (2)	0.0452 (19)	0.0296 (16)	0.0060 (15)	−0.0076 (14)	0.0109 (14)
C214	0.0395 (18)	0.0333 (17)	0.050 (2)	0.0082 (14)	−0.0018 (15)	0.0176 (14)
C215	0.0339 (17)	0.0204 (14)	0.060 (2)	0.0030 (12)	0.0092 (15)	0.0008 (13)
C216	0.0256 (14)	0.0230 (14)	0.0350 (15)	0.0005 (11)	0.0045 (12)	−0.0054 (11)
N22	0.0165 (10)	0.0232 (11)	0.0215 (10)	−0.0014 (8)	0.0014 (8)	−0.0022 (8)
C23	0.0227 (13)	0.0210 (13)	0.0183 (12)	−0.0032 (10)	−0.0035 (10)	−0.0020 (9)
C231	0.0284 (15)	0.0287 (15)	0.0326 (15)	0.0004 (12)	0.0076 (12)	0.0042 (12)
C24	0.0206 (12)	0.0161 (11)	0.0180 (11)	−0.0010 (9)	−0.0047 (9)	−0.0006 (9)
S21	0.0251 (4)	0.0200 (3)	0.0306 (4)	0.0028 (3)	−0.0061 (3)	−0.0013 (3)
C22	0.0192 (12)	0.0198 (12)	0.0224 (12)	0.0016 (10)	0.0002 (10)	−0.0016 (10)
C221	0.0242 (13)	0.0178 (12)	0.0208 (12)	0.0034 (10)	−0.0029 (10)	−0.0053 (9)
C222	0.0354 (16)	0.0360 (16)	0.0195 (13)	−0.0008 (12)	−0.0023 (11)	−0.0050 (11)
C223	0.055 (2)	0.0411 (18)	0.0273 (15)	0.0046 (15)	−0.0163 (14)	−0.0060 (13)
C224	0.0421 (18)	0.0310 (16)	0.0435 (17)	0.0071 (13)	−0.0230 (14)	−0.0128 (13)
C225	0.0208 (13)	0.0246 (14)	0.0464 (17)	0.0017 (11)	−0.0083 (12)	−0.0101 (12)
C226	0.0231 (13)	0.0244 (13)	0.0278 (14)	0.0020 (10)	−0.0036 (11)	−0.0018 (10)
N23	0.0243 (11)	0.0165 (10)	0.0197 (10)	−0.0008 (8)	−0.0054 (8)	−0.0003 (8)

C241	0.0268 (14)	0.0244 (13)	0.0228 (13)	−0.0052 (11)	−0.0075 (11)	0.0031 (10)
O24	0.0496 (13)	0.0284 (11)	0.0227 (10)	0.0004 (9)	−0.0117 (9)	−0.0009 (8)
C251	0.0274 (14)	0.0245 (14)	0.0310 (14)	0.0018 (11)	−0.0116 (11)	0.0013 (11)
C25	0.0176 (12)	0.0188 (12)	0.0196 (12)	−0.0020 (9)	−0.0050 (9)	−0.0010 (9)
N25	0.0190 (11)	0.0205 (11)	0.0284 (11)	0.0004 (8)	−0.0012 (9)	0.0042 (9)

Geometric parameters (Å, º)

N11—C15	1.353 (3)	N21—C25	1.346 (3)
N11—N12	1.388 (3)	N21—N22	1.383 (3)
N11—C111	1.425 (3)	N21—C211	1.428 (3)
C111—C116	1.378 (3)	C211—C216	1.378 (4)
C111—C112	1.393 (3)	C211—C212	1.384 (4)
C112—C113	1.381 (4)	C212—C213	1.390 (4)
C112—H112	0.95	C212—H212	0.95
C113—C114	1.386 (4)	C213—C214	1.377 (5)
C113—H113	0.95	C213—H213	0.95
C114—C115	1.386 (4)	C214—C215	1.373 (5)
C114—H114	0.95	C214—H214	0.95
C115—C116	1.387 (4)	C215—C216	1.393 (4)
C115—H115	0.95	C215—H215	0.95
C116—H116	0.95	C216—H216	0.95
N12—C13	1.333 (3)	N22—C23	1.327 (3)
C13—C14	1.401 (3)	C23—C24	1.407 (4)
C13—C131	1.494 (4)	C23—C231	1.486 (3)
C131—H13A	0.98	C231—H23A	0.98
C131—H13B	0.98	C231—H23B	0.98
C131—H13C	0.98	C231—H23C	0.98
C14—C15	1.383 (3)	C24—C25	1.392 (3)
C14—N13	1.421 (3)	C24—N23	1.411 (3)
S11—C12	1.830 (2)	S21—C22	1.828 (2)
S11—C151	1.796 (3)	S21—C251	1.795 (3)
C12—N13	1.465 (3)	C22—N23	1.473 (3)
C12—C121	1.509 (3)	C22—C221	1.514 (3)
C12—H12	1.00	C22—H22	1.00
C121—C126	1.387 (4)	C221—C222	1.385 (3)
C121—C122	1.390 (4)	C221—C226	1.389 (4)
C122—C123	1.393 (5)	C222—C223	1.397 (4)
C122—H122	0.95	C222—H222	0.95
C123—C124	1.365 (6)	C223—C224	1.380 (5)
C123—H123	0.95	C223—H223	0.95
C124—C125	1.391 (5)	C224—C225	1.384 (4)
C124—H124	0.95	C224—H224	0.95
C125—C126	1.377 (4)	C225—C226	1.382 (4)
C125—H125	0.95	C225—H225	0.95
C126—H126	0.95	C226—H226	0.95
N13—C141	1.364 (3)	N23—C241	1.358 (3)
C141—O14	1.221 (3)	C241—O24	1.221 (3)

C141—C151	1.510 (4)	C241—C251	1.512 (4)
C151—H15C	0.99	C251—H25C	0.99
C151—H15D	0.99	C251—H25D	0.99
C15—N15	1.379 (3)	C25—N25	1.375 (3)
N15—H15A	0.88	N25—H25A	0.88
N15—H15B	0.88	N25—H25B	0.88
C15—N11—N12	112.16 (19)	C25—N21—N22	112.92 (19)
C15—N11—C111	128.6 (2)	C25—N21—C211	127.6 (2)
N12—N11—C111	118.62 (19)	N22—N21—C211	118.9 (2)
C116—C111—C112	121.3 (2)	C216—C211—C212	121.5 (2)
C116—C111—N11	119.5 (2)	C216—C211—N21	119.5 (2)
C112—C111—N11	119.2 (2)	C212—C211—N21	119.0 (2)
C113—C112—C111	119.2 (3)	C211—C212—C213	119.3 (3)
C113—C112—H112	120.4	C211—C212—H212	120.4
C111—C112—H112	120.4	C213—C212—H212	120.4
C112—C113—C114	120.1 (3)	C214—C213—C212	119.4 (3)
C112—C113—H113	120.0	C214—C213—H213	120.3
C114—C113—H113	120.0	C212—C213—H213	120.3
C115—C114—C113	120.1 (3)	C215—C214—C213	121.0 (3)
C115—C114—H114	120.0	C215—C214—H214	119.5
C113—C114—H114	120.0	C213—C214—H214	119.5
C114—C115—C116	120.4 (3)	C214—C215—C216	120.2 (3)
C114—C115—H115	119.8	C214—C215—H215	119.9
C116—C115—H115	119.8	C216—C215—H215	119.9
C111—C116—C115	119.0 (2)	C211—C216—C215	118.6 (3)
C111—C116—H116	120.5	C211—C216—H216	120.7
C115—C116—H116	120.5	C215—C216—H216	120.7
C13—N12—N11	104.19 (19)	C23—N22—N21	104.13 (19)
N12—C13—C14	111.5 (2)	N22—C23—C24	111.5 (2)
N12—C13—C131	120.4 (2)	N22—C23—C231	120.9 (2)
C14—C13—C131	128.1 (2)	C24—C23—C231	127.5 (2)
C13—C131—H13A	109.5	C23—C231—H23A	109.5
C13—C131—H13B	109.5	C23—C231—H23B	109.5
H13A—C131—H13B	109.5	H23A—C231—H23B	109.5
C13—C131—H13C	109.5	C23—C231—H23C	109.5
H13A—C131—H13C	109.5	H23A—C231—H23C	109.5
H13B—C131—H13C	109.5	H23B—C231—H23C	109.5
C15—C14—C13	106.1 (2)	C25—C24—C23	105.8 (2)
C15—C14—N13	125.7 (2)	C25—C24—N23	126.0 (2)
C13—C14—N13	128.0 (2)	C23—C24—N23	127.8 (2)
C151—S11—C12	91.17 (11)	C251—S21—C22	91.52 (12)
N13—C12—C121	112.4 (2)	N23—C22—C221	111.0 (2)
N13—C12—S11	104.04 (15)	N23—C22—S21	104.60 (15)
C121—C12—S11	110.20 (17)	C221—C22—S21	110.85 (17)
N13—C12—H12	110.0	N23—C22—H22	110.1
C121—C12—H12	110.0	C221—C22—H22	110.1
S11—C12—H12	110.0	S21—C22—H22	110.1

C126—C121—C122	119.2 (3)	C222—C221—C226	119.6 (2)
C126—C121—C12	120.9 (2)	C222—C221—C22	120.0 (2)
C122—C121—C12	119.9 (3)	C226—C221—C22	120.4 (2)
C121—C122—C123	120.0 (3)	C221—C222—C223	119.9 (3)
C121—C122—H122	120.0	C221—C222—H222	120.1
C123—C122—H122	120.0	C223—C222—H222	120.1
C124—C123—C122	120.1 (3)	C224—C223—C222	119.8 (3)
C124—C123—H123	119.9	C224—C223—H223	120.1
C122—C123—H123	119.9	C222—C223—H223	120.1
C123—C124—C125	120.3 (3)	C223—C224—C225	120.5 (3)
C123—C124—H124	119.8	C223—C224—H224	119.8
C125—C124—H124	119.8	C225—C224—H224	119.8
C126—C125—C124	119.7 (3)	C226—C225—C224	119.6 (3)
C126—C125—H125	120.1	C226—C225—H225	120.2
C124—C125—H125	120.1	C224—C225—H225	120.2
C125—C126—C121	120.6 (3)	C225—C226—C221	120.6 (2)
C125—C126—H126	119.7	C225—C226—H226	119.7
C121—C126—H126	119.7	C221—C226—H226	119.7
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)
O14—C141—N13	124.4 (2)	O24—C241—N23	124.3 (2)
O14—C141—C151	124.4 (2)	O24—C241—C251	124.2 (2)
N13—C141—C151	111.2 (2)	N23—C241—C251	111.5 (2)
C141—C151—S11	107.23 (17)	C241—C251—S21	107.60 (17)
C141—C151—H15C	110.3	C241—C251—H25C	110.2
S11—C151—H15C	110.3	S21—C251—H25C	110.2
C141—C151—H15D	110.3	C241—C251—H25D	110.2
S11—C151—H15D	110.3	S21—C251—H25D	110.2
H15C—C151—H15D	108.5	H25C—C251—H25D	108.5
N11—C15—N15	123.6 (2)	N21—C25—N25	124.2 (2)
N11—C15—C14	106.1 (2)	N21—C25—C24	105.6 (2)
N15—C15—C14	130.3 (2)	N25—C25—C24	130.1 (2)
C15—N15—H15A	109.7	C25—N25—H25A	112.2
C15—N15—H15B	118.1	C25—N25—H25B	117.4
H15A—N15—H15B	104.9	H25A—N25—H25B	110.2

C15—N11—C111—C116	−127.2 (3)	C25—N21—C211—C216	121.4 (3)
N12—N11—C111—C116	62.2 (3)	N22—N21—C211—C216	−68.1 (3)
C15—N11—C111—C112	54.6 (4)	C25—N21—C211—C212	−61.0 (4)
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)
C116—C111—C112—C113	−0.3 (4)	C216—C211—C212—C213	−0.9 (4)
N11—C111—C112—C113	177.8 (2)	N21—C211—C212—C213	−178.4 (3)
C111—C112—C113—C114	−0.7 (4)	C211—C212—C213—C214	1.2 (5)
C112—C113—C114—C115	1.0 (5)	C212—C213—C214—C215	−0.6 (5)
C113—C114—C115—C116	−0.1 (4)	C213—C214—C215—C216	−0.1 (5)
C112—C111—C116—C115	1.1 (4)	C212—C211—C216—C215	0.2 (4)

N11—C111—C116—C115	−177.0 (2)	N21—C211—C216—C215	177.6 (2)
C114—C115—C116—C111	−0.9 (4)	C214—C215—C216—C211	0.4 (4)
C15—N11—N12—C13	0.2 (3)	C25—N21—N22—C23	0.0 (3)
C111—N11—N12—C13	172.3 (2)	C211—N21—N22—C23	−171.8 (2)
N11—N12—C13—C14	−0.4 (3)	N21—N22—C23—C24	−0.1 (3)
N11—N12—C13—C131	178.9 (2)	N21—N22—C23—C231	−179.5 (2)
N12—C13—C14—C15	0.4 (3)	N22—C23—C24—C25	0.2 (3)
C131—C13—C14—C15	−178.8 (2)	C231—C23—C24—C25	179.5 (2)
N12—C13—C14—N13	−174.0 (2)	N22—C23—C24—N23	173.1 (2)
C131—C13—C14—N13	6.8 (4)	C231—C23—C24—N23	−7.6 (4)
C151—S11—C12—N13	−26.86 (18)	C251—S21—C22—N23	24.17 (18)
C151—S11—C12—C121	−147.52 (18)	C251—S21—C22—C221	143.82 (19)
N13—C12—C121—C126	−49.9 (3)	N23—C22—C221—C222	−119.1 (3)
S11—C12—C121—C126	65.6 (3)	S21—C22—C221—C222	125.1 (2)
N13—C12—C121—C122	131.5 (3)	N23—C22—C221—C226	59.9 (3)
S11—C12—C121—C122	−112.9 (2)	S21—C22—C221—C226	−55.9 (3)
C126—C121—C122—C123	0.8 (4)	C226—C221—C222—C223	0.4 (4)
C12—C121—C122—C123	179.4 (3)	C22—C221—C222—C223	179.3 (3)
C121—C122—C123—C124	0.1 (5)	C221—C222—C223—C224	0.1 (4)
C122—C123—C124—C125	−1.1 (5)	C222—C223—C224—C225	−0.5 (4)
C123—C124—C125—C126	1.2 (5)	C223—C224—C225—C226	0.6 (4)
C124—C125—C126—C121	−0.3 (4)	C224—C225—C226—C221	−0.1 (4)
C122—C121—C126—C125	−0.7 (4)	C222—C221—C226—C225	−0.3 (4)
C12—C121—C126—C125	−179.3 (2)	C22—C221—C226—C225	−179.3 (2)
C15—C14—N13—C141	120.1 (3)	C25—C24—N23—C241	−120.6 (3)
C13—C14—N13—C141	−66.6 (3)	C23—C24—N23—C241	67.9 (3)
C15—C14—N13—C12	−51.6 (3)	C25—C24—N23—C22	53.7 (3)
C121—C12—N13—C141	142.5 (2)	C221—C22—N23—C241	−140.1 (2)
S11—C12—N13—C141	23.3 (3)	S21—C22—N23—C241	−20.5 (3)
C121—C12—N13—C14	−45.3 (3)	C221—C22—N23—C24	45.2 (3)
S11—C12—N13—C14	−164.52 (17)	S21—C22—N23—C24	164.80 (17)
C14—N13—C141—O14	2.9 (4)	C24—N23—C241—O24	−2.3 (4)
C12—N13—C141—O14	174.8 (2)	C22—N23—C241—O24	−176.6 (2)
C14—N13—C141—C151	−176.9 (2)	C24—N23—C241—C251	178.1 (2)
C12—N13—C141—C151	−5.1 (3)	C22—N23—C241—C251	3.7 (3)
O14—C141—C151—S11	163.8 (2)	O24—C241—C251—S21	−164.2 (2)
N13—C141—C151—S11	−16.4 (3)	N23—C241—C251—S21	15.5 (3)
C12—S11—C151—C141	25.16 (19)	C22—S21—C251—C241	−23.0 (2)
N12—N11—C15—N15	178.5 (2)	N22—N21—C25—N25	−177.5 (2)
C111—N11—C15—N15	7.4 (4)	C211—N21—C25—N25	−6.5 (4)
N12—N11—C15—C14	0.0 (3)	N22—N21—C25—C24	0.1 (3)
C111—N11—C15—C14	−171.0 (2)	C211—N21—C25—C24	171.1 (2)
C13—C14—C15—N11	−0.2 (3)	C23—C24—C25—N21	−0.2 (3)
N13—C14—C15—N11	174.3 (2)	N23—C24—C25—N21	−173.2 (2)
C13—C14—C15—N15	−178.5 (2)	C23—C24—C25—N25	177.2 (2)
N13—C14—C15—N15	−4.0 (4)	N23—C24—C25—N25	4.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N15—H15*A*···N22	0.88	2.20	3.077 (3)	172
N25—H25*A*···N12^{i}	0.88	2.20	3.064 (3)	165

Symmetry code: (i) *x*−1, *y*, *z*.