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4,5,6-Triamino-2-(methylsulfanyl)-pyrimidine: π-stacked hydrogen-bonded sheets of $R_2^2(8)$, $R_2^2(10)$ and $R_6^6(32)$ rings

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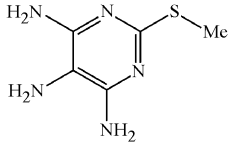
In the title compound, $C_5H_9N_5S$, the three independent C—NH_2 units are all somewhat pyramidal. The molecules are linked by a combination of one N—H···S and two N—H···N hydrogen bonds into sheets containing three types of ring motif, *viz.* $R_2^2(8)$, $R_2^2(10)$ and $R_6^6(32)$, all of them centrosymmetric. Adjacent sheets are linked by a single π–π stacking interaction.

Comment

The title compound, (I), was prepared following a published procedure (Baddiley *et al.*, 1943) for use as an intermediate in the synthesis of fused pyrimidine derivatives of potential biological interest.



(I)

Within the heterocyclic ring in the molecule of (I), the bond distances (Table 1) provide evidence for aromatic delocalization. The internal bond angles at atoms N1, N3 and C5 are all significantly less than the idealized value of 120°; those at N1 and N3 reflect the stereochemical influence of the lone pairs of electrons on these atoms, while that at C5 is influenced by the behaviour of the exocyclic amino group.

Each of the three independent C—NH_2 units is, to a greater or lesser extent, pyramidal, and this is least marked for atom N6 and most marked for atom N5. The sums of the interbond angles at atoms N4, N5 and N6 deviate by 12, 26 and 3°, respectively, from 360°. Closely associated with the degree of pyramidalization at the amino N atoms is the variation in the exocyclic C—N bond distances (Table 1), with C5—N5 the longest of these and C6—N6 the shortest. The very long C5—N5 bond is also doubtless influenced by the rotation of the lone pair at N5 to be almost coplanar with the pyrimidine ring (Table 1 and Fig. 1). The mean values (Allen *et al.*, 1987) for C—S bonds of the types found in (I) are 1.773 and 1.789 Å, so that the difference between the S2—C2 and S2—C21 distances is larger than expected.

Amino atoms N4 and N5 are, therefore, potential acceptors of hydrogen bonds, in addition to ring atoms N1 and N3 and sulfanyl atom S2, while each amino group is potentially a double donor of hydrogen bonds. In practice, there is one intramolecular N—H···N hydrogen bond (Table 2), with the highly pyramidal N5 atom as the acceptor, and each amino group acts as a single donor in intermolecular hydrogen bonds, with one ring N atom, one amino N atom and the S atom as the

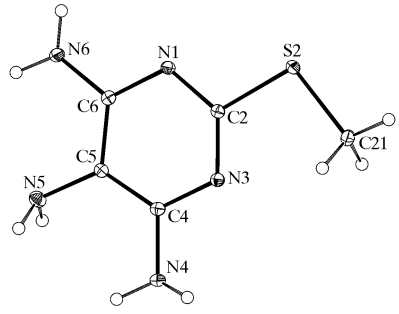


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displdisplacement ellipsoids are drawn at the 30% probability level.

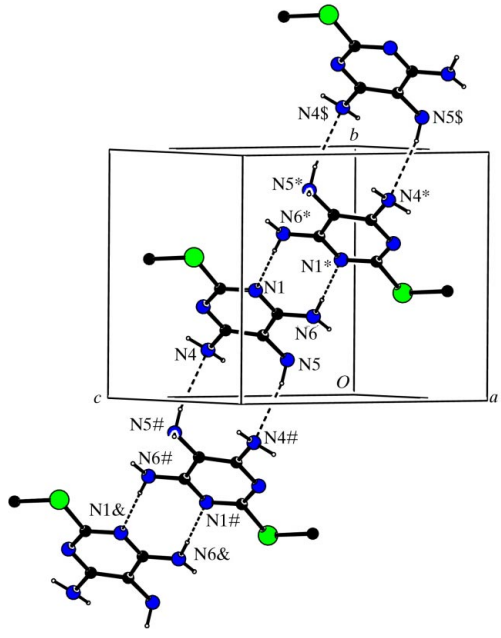


Figure 2
Part of the crystal structure of (I), showing a chain of alternating $R_2^2(8)$ and $R_2^2(10)$ rings along [110]. For the sake of clarity, the H atoms of the methyl group have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(-x, -y, 1-z)$, $(1+x, 1+y, z)$ and $(-1+x, -1+y, z)$, respectively.

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three acceptors (Table 2). Hence, two of the N—H bonds do not participate in any hydrogen-bond formation.

The three intermolecular hydrogen bonds generate a sheet containing three distinct types of ring, all centrosymmetric, but the formation of this rather complex sheet is readily analysed in terms of two straightforward one-dimensional substructures, one built from two independent N—H···N hydrogen bonds and the other built using only N—H···S hydrogen bonds.

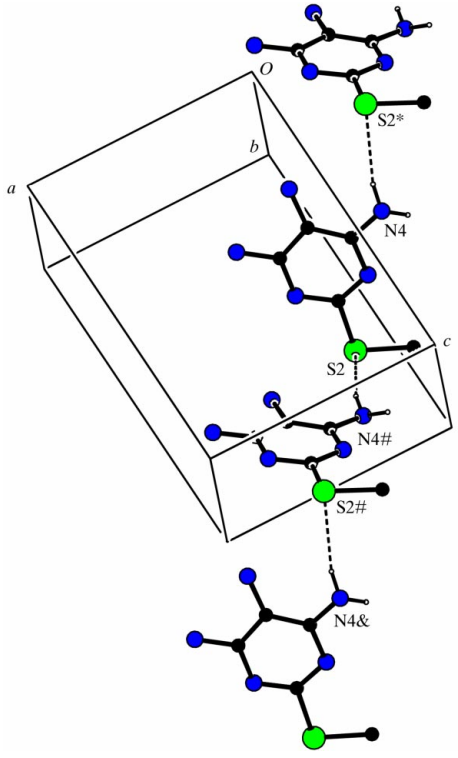

Figure 3
Part of the crystal structure of (I), showing a $C(6)$ chain along [101]. For the sake of clarity, H atoms bonded to C or N atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(1+x, y, 1+z)$, respectively.

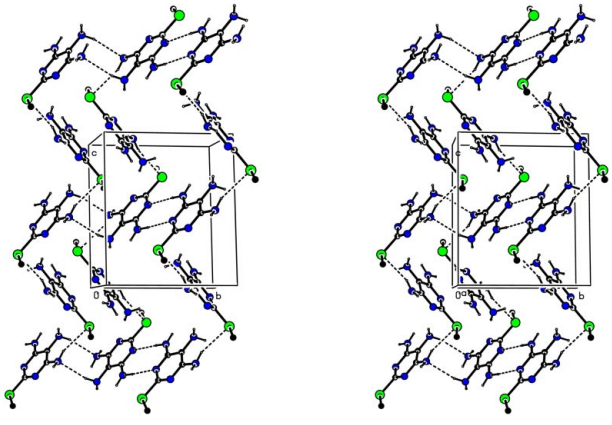

Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a $(\bar{1}11)$ sheet of $R_2^2(8)$, $R_2^2(10)$ and $R_6^6(32)$ rings. For the sake of clarity, the H atoms of the methyl group have been omitted.

Amino atom N5 in the molecule at (x, y, z) acts as hydrogen-bond donor to the pyramidal amino N4 atom in the molecule at $(-x, -y, 1-z)$, so forming a centrosymmetric $R_2^2(10)$ (Bernstein *et al.*, 1995) ring centred at $(0, 0, \frac{1}{2})$. Similarly, amino atom N6 at (x, y, z) acts as hydrogen-bond donor to ring atom N1 in the molecule at $(1-x, 1-y, 1-z)$, so forming a second ring motif, this time of $R_2^2(8)$ type, centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation by inversion of these two hydrogen bonds then generates a chain of centrosymmetric rings running parallel to the [110] direction, with $R_2^2(8)$ rings centred at $(n+\frac{1}{2}, n+\frac{1}{2}, \frac{1}{2})$ (n = zero or integer) and $R_2^2(10)$ rings centred at $(n, n, \frac{1}{2})$ (n = zero or integer) (Fig. 2).

In the second one-dimensional substructure, amino atom N4 in the molecule at (x, y, z) acts as hydrogen-bond donor to the S atom in the molecule at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, thereby forming a $C(6)$ chain running parallel to the [101] direction and generated by the n-glide plane at $y = \frac{1}{4}$ (Fig. 3).

The combination of the [110] and [101] chains generates a $(\bar{1}11)$ sheet built from $R_2^2(8)$, $R_2^2(10)$ and $R_6^6(32)$ rings, all of them centrosymmetric (Fig. 4), and these sheets are linked by a centrosymmetric π–π stacking interaction. The pyrimidine rings of the molecules at (x, y, z) and $(-x, 1-y, 1-z)$ are strictly parallel, with an interplanar spacing of 3.337 (2) Å. The ring-centroid separation is 3.649 (2) Å, corresponding to a near-ideal ring offset of 1.476 (2) Å. The combination of this interaction with the $R_2^2(8)$ rings generates a chain running parallel to the [100] direction, while the combination of the π-stacking interaction with the $R_2^2(10)$ rings generates a chain parallel to the [010] direction. In this manner, the $(\bar{1}11)$ sheets are linked into a single three-dimensional structure.

Experimental

Crystals of the title compound, (I), were prepared according to the procedure of Baddiley *et al.* (1943).

Crystal data

$C_5H_9N_5S$
$M_r = 171.23$
Monoclinic, $P2_1/n$
$a = 7.7824$ (2) Å
$b = 8.9623$ (3) Å
$c = 10.5078$ (4) Å
$\beta = 95.261$ (2)°
$V = 729.81$ (4) Å^3
$Z = 4$
$D_x = 1.558$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1659 reflections
$\theta = 3.9$–27.5°
$\mu = 0.38$ mm^{-1}
$T = 120$ (2) K
Rod, yellow
0.40 × 0.20 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.863$, $T_{max} = 0.963$
9338 measured reflections
1659 independent reflections
1533 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.073$
$S = 1.11$
1659 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 0.4621P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.3337 (16)	C4—N4	1.3759 (16)
C2—N3	1.3242 (16)	C5—N5	1.4292 (16)
N3—C4	1.3573 (17)	C6—N6	1.3518 (16)
C4—C5	1.3888 (18)	C2—S2	1.7694 (13)
C5—C6	1.4104 (17)	S2—C21	1.7997 (13)
C6—N1	1.3557 (16)		
C6—N1—C2	115.40 (11)	N1—C2—S2	112.03 (9)
N1—C2—N3	129.07 (11)	N3—C2—S2	118.90 (9)
C2—N3—C4	114.55 (11)	C2—S2—C21	101.71 (6)
N3—C4—C5	123.14 (11)	C4—N4—H4*A*	114.9
C4—C5—C6	116.22 (11)	C4—N4—H4*B*	111.4
C5—C6—N1	121.60 (11)	H4*A*—N4—H4*B*	118.1
N3—C4—N4	114.95 (11)	C5—N5—H5*A*	112.1
C5—C4—N4	121.88 (12)	C5—N5—H5*B*	113.7
C4—C5—N5	124.73 (11)	H5*A*—N5—H5*B*	108.0
C6—C5—N5	119.04 (11)	C6—N6—H6*A*	117.9
C5—C6—N6	121.56 (11)	C6—N6—H6*B*	119.2
N1—C6—N6	116.82 (11)	H6*A*—N6—H6*B*	119.7
N3—C4—N4—H4*A*	163	N3—C4—N4—H4*B*	26
C4—C5—N5—H5*A*	−69	C4—C5—N5—H5*B*	54
C5—C6—N6—H6*A*	170	C5—C6—N6—H6*B*	10

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···S2^{i}	0.88	2.75	3.5902 (12)	159
N5—H5*A*···N4^{ii}	0.88	2.48	3.3379 (16)	166
N6—H6*A*···N1^{iii}	0.88	2.23	3.1049 (15)	176
N6—H6*B*···N5	0.88	2.48	2.8134 (16)	103

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

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms. The H atoms of the methyl group were assigned C—H distances of 0.98 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$. The amino H atoms were allowed to ride at the locations deduced from the difference maps, with N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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: SK1899). 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.
Baddiley, J., Lythgoe, B., McNeil, D. & Todd, A. R. (1943). *J. Chem. Soc.* pp. 383–386.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Nonius (1999). *COLLECT*. 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.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.