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4-Hydrazino-2-(methylsulfanyl)-pyrimidine

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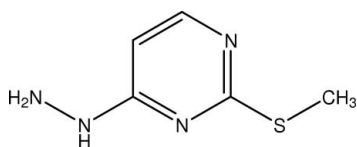
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 30.4.

In the crystal of the title compound, $\text{C}_5\text{H}_8\text{N}_4$, centrosymmetric dimers are linked by pairs of $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. Further $\text{N}-\text{H}\cdots\text{N}$ links result in a two-dimensional array whereby wave-like supramolecular chains are interconnected by $R_2^2(8)$ ring motifs.

Related literature

For general background, see: Ghorab *et al.* (2004); Anderson *et al.* (1990); Géza *et al.* (2001); Gante (1989); Powers *et al.* (1998); Vidrio *et al.* (2003). For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_5\text{H}_8\text{N}_4\text{S}$
 $M_r = 156.21$
Orthorhombic, $Pbca$
 $a = 12.7906$ (2) Å
 $b = 7.7731$ (1) Å
 $c = 14.4354$ (3) Å

$V = 1435.21$ (4) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.38$ mm⁻¹
 $T = 100.0$ (1) K
 $0.55 \times 0.37 \times 0.17$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)
 $T_{\min} = 0.821$, $T_{\max} = 0.938$
16377 measured reflections

3160 independent reflections
2760 reflections with $I > 2\sigma(I)$

 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.05$
3160 reflections
104 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| $\text{N3}-\text{H1N3}\cdots\text{N1}^i$ | 0.84 (2) | 2.24 (2) | 3.070 (1) | 172 (1) |
| $\text{N4}-\text{H1N4}\cdots\text{N2}^{ii}$ | 0.82 (2) | 2.42 (2) | 3.208 (1) | 161 (1) |
| $\text{N4}-\text{H2N4}\cdots\text{N2}^{iii}$ | 0.89 (1) | 2.30 (2) | 3.137 (1) | 157 (1) |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2360).

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supporting information

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4-Hydrazino-2-(methylsulfanyl)pyrimidine

Hoong-Kun Fun, Ibrahim Abdul Razak, Adithya Adhikari and Balakrishna Kalluraya

S1. Comment

Pyrimidines and their derivatives possess biological and pharmacological activities such as antibacterial, antimicrobial, anti-inflammatory, analgesic, anticonvulsant and anti-aggressive activities (Ghorab *et al.*, 2004; Anderson *et al.*, 1990). This prompted us to synthesize compounds bearing the pyrimidine moiety. Hydrazine derivatives are interesting building blocks of heterocyclic compounds containing N—N bonds (Geza *et al.*, 1981; Gante, 1989). Some hydrazine derivatives such as phthalazin-1-yl-hydrazine are widely used as general antihypertensive and vasodilator agents, and are considered as a first-line drug in the management of pregnancy-induced hypertension (Powers *et al.*, 1998; Vidrio *et al.*, 2003). In addition, these compounds are known to decompose easily in the presence of radicals into hydrazine derivatives which are commonly used as rocket fuels. The structure of the title compound, (I), was determined in this context. The molecule of (I), Fig. 1, is essentially planar, with the maximum deviation from the least-squares plane being 0.297 (1) Å for the C5 atom.

The primary interactions in the crystal structure are of the type N—H···N, Table 1 and Fig. 2. Here, molecules form wave-like supramolecular chains along the *b* axis with successive molecules connected on either side via $R_2^2(8)$ motifs (Bernstein *et al.*, 1995) to form a 2-D array.

S2. Experimental

4-Chloro-2-(methylsulfanyl)pyrimidine (0.01 mol) was dissolved in methanol and 99% hydrazine hydrate (0.015 mol) was added dropwise with external cooling. The mixture was stirred at room temperature for 5 h. The precipitate was filtered, dried and recrystallized from ethyl acetate. Crystals suitable for X-ray studies are obtained from ethyl acetate by slow evaporation. Yield 65%, m.p. 413 K.

S3. Refinement

All H atoms were positioned geometrically and refined with a riding model approximation with C—H = 0.93–0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The rotating model group was employed for the methyl group. In the case of N3 and N4 atoms, the H atoms were located from a difference Fourier map and refined isotropically, see Table 1 for bond distances.

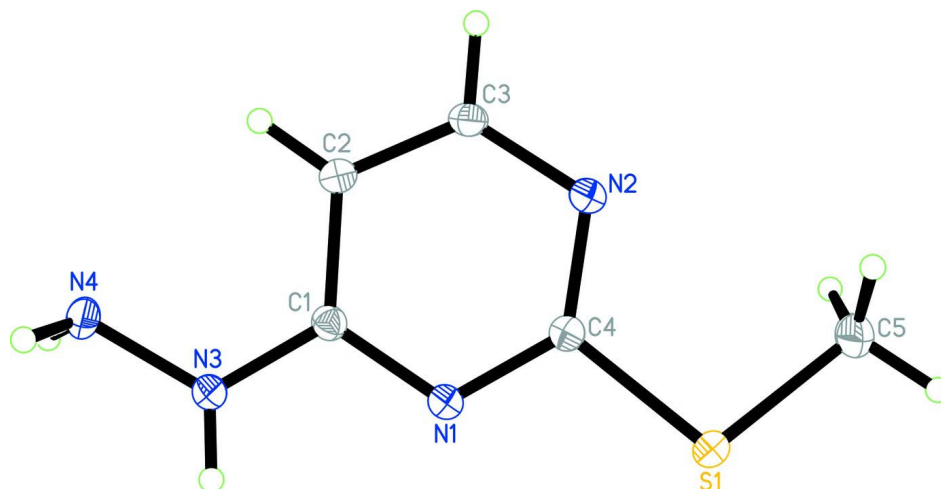


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

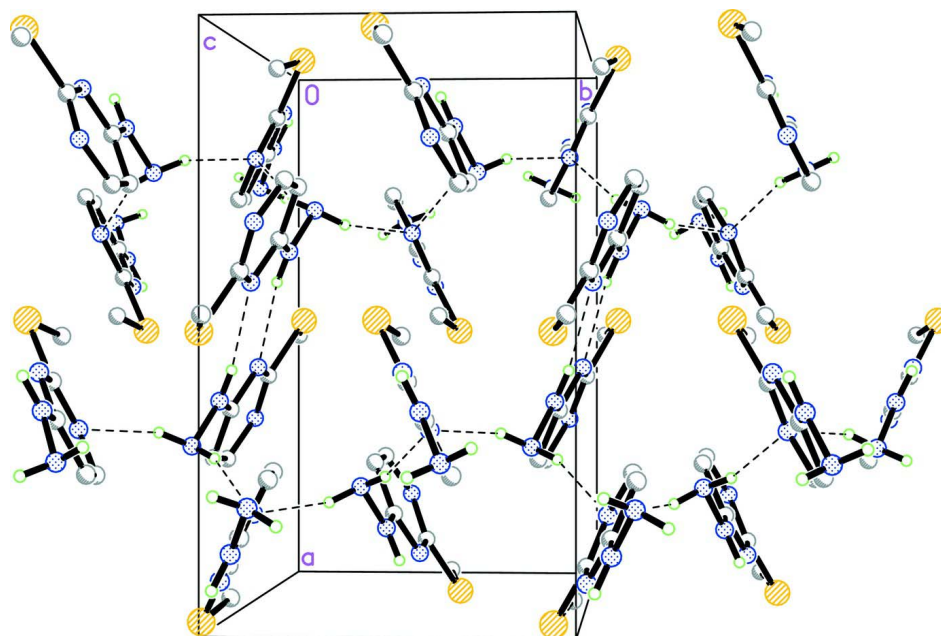


Figure 2

A view of the crystal packing in (I), viewed down the *c* axis, showing wave-like chains along the *b* axis. H atoms involved in hydrogen bonds are shown as dotted lines. Other H atoms have been omitted for clarity.

4-Hydrazino-2-(methylsulfonyl)pyrimidine

Crystal data

$C_5H_8N_4S$

$M_r = 156.21$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 12.7906 (2) \text{ \AA}$

$b = 7.7731 (1) \text{ \AA}$

$c = 14.4354 (3) \text{ \AA}$

$V = 1435.21 (4) \text{ \AA}^3$

$Z = 8$

$F(000) = 656$

$D_x = 1.446 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6385 reflections

$\theta = 3.2\text{--}38.6^\circ$

$\mu = 0.38 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Block, colourless
 $0.55 \times 0.37 \times 0.17 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.821, T_{\max} = 0.938$

16377 measured reflections
 3160 independent reflections
 2760 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 35.0^\circ, \theta_{\min} = 2.8^\circ$
 $h = -20 \rightarrow 19$
 $k = -12 \rightarrow 10$
 $l = -15 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.05$
 3160 reflections
 104 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.4069P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The data was collected with the Oxford Cryosystem Cobra low-temperature attachment

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 | 0.009609 (17) | 0.58095 (3) | 0.239703 (15) | 0.01516 (6) |
| N1 | -0.07742 (5) | 0.47877 (10) | 0.39095 (5) | 0.01315 (13) |
| N2 | -0.17805 (6) | 0.42798 (10) | 0.25325 (5) | 0.01321 (13) |
| N3 | -0.13619 (6) | 0.40510 (11) | 0.53498 (5) | 0.01709 (15) |
| N4 | -0.21443 (6) | 0.34229 (11) | 0.59510 (5) | 0.01670 (14) |
| C1 | -0.15419 (6) | 0.40931 (10) | 0.44356 (6) | 0.01236 (14) |
| C2 | -0.24631 (6) | 0.34361 (11) | 0.40217 (6) | 0.01379 (14) |
| H2A | -0.2994 | 0.2943 | 0.4373 | 0.017* |
| C3 | -0.25315 (6) | 0.35641 (11) | 0.30784 (6) | 0.01370 (14) |
| H3A | -0.3128 | 0.3135 | 0.2792 | 0.016* |
| C4 | -0.09458 (6) | 0.48345 (10) | 0.29943 (5) | 0.01199 (13) |
| C5 | -0.01837 (8) | 0.53439 (15) | 0.12034 (7) | 0.02202 (19) |

| | | | | |
|------|--------------|-------------|-------------|------------|
| H5A | 0.0365 | 0.5797 | 0.0820 | 0.033* |
| H5B | -0.0836 | 0.5865 | 0.1033 | 0.033* |
| H5C | -0.0229 | 0.4121 | 0.1119 | 0.033* |
| H1N3 | -0.0801 (12) | 0.4477 (18) | 0.5550 (10) | 0.027 (4)* |
| H1N4 | -0.2343 (11) | 0.420 (2) | 0.6293 (10) | 0.025 (4)* |
| H2N4 | -0.1890 (10) | 0.2573 (19) | 0.6296 (10) | 0.024 (3)* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|--------------|--------------|--------------|--------------|-------------|-------------|
| S1 | 0.01382 (10) | 0.01761 (11) | 0.01405 (10) | -0.00356 (7) | 0.00068 (6) | 0.00078 (7) |
| N1 | 0.0126 (3) | 0.0153 (3) | 0.0115 (3) | -0.0011 (2) | -0.0007 (2) | -0.0003 (2) |
| N2 | 0.0126 (3) | 0.0147 (3) | 0.0123 (3) | -0.0004 (2) | -0.0012 (2) | -0.0003 (2) |
| N3 | 0.0135 (3) | 0.0266 (4) | 0.0111 (3) | -0.0045 (3) | -0.0009 (2) | 0.0012 (3) |
| N4 | 0.0149 (3) | 0.0223 (4) | 0.0129 (3) | -0.0009 (3) | 0.0026 (2) | 0.0012 (3) |
| C1 | 0.0119 (3) | 0.0134 (3) | 0.0117 (3) | 0.0008 (2) | -0.0004 (2) | -0.0003 (3) |
| C2 | 0.0119 (3) | 0.0155 (3) | 0.0140 (3) | -0.0016 (3) | -0.0004 (2) | -0.0001 (3) |
| C3 | 0.0118 (3) | 0.0150 (3) | 0.0143 (3) | -0.0007 (3) | -0.0017 (2) | -0.0008 (3) |
| C4 | 0.0119 (3) | 0.0117 (3) | 0.0123 (3) | 0.0006 (2) | 0.0001 (2) | -0.0003 (2) |
| C5 | 0.0187 (4) | 0.0334 (5) | 0.0139 (4) | -0.0036 (4) | 0.0017 (3) | 0.0008 (3) |

Geometric parameters (Å, °)

| | | | |
|--------------|-------------|------------|-------------|
| S1—C4 | 1.7589 (8) | N4—H1N4 | 0.822 (15) |
| S1—C5 | 1.7967 (10) | N4—H2N4 | 0.889 (15) |
| N1—C4 | 1.3397 (10) | C1—C2 | 1.4164 (11) |
| N1—C1 | 1.3537 (11) | C2—C3 | 1.3681 (12) |
| N2—C4 | 1.3305 (11) | C2—H2A | 0.9300 |
| N2—C3 | 1.3613 (11) | C3—H3A | 0.9300 |
| N3—C1 | 1.3399 (11) | C5—H5A | 0.9600 |
| N3—N4 | 1.4118 (11) | C5—H5B | 0.9600 |
| N3—H1N3 | 0.841 (15) | C5—H5C | 0.9600 |
| C4—S1—C5 | 103.44 (4) | C1—C2—H2A | 121.7 |
| C4—N1—C1 | 116.44 (7) | N2—C3—C2 | 124.11 (8) |
| C4—N2—C3 | 114.11 (7) | N2—C3—H3A | 117.9 |
| C1—N3—N4 | 119.48 (7) | C2—C3—H3A | 117.9 |
| C1—N3—H1N3 | 118.4 (10) | N2—C4—N1 | 128.08 (8) |
| N4—N3—H1N3 | 121.9 (10) | N2—C4—S1 | 120.13 (6) |
| N3—N4—H1N4 | 109.5 (10) | N1—C4—S1 | 111.77 (6) |
| N3—N4—H2N4 | 110.0 (9) | S1—C5—H5A | 109.5 |
| H1N4—N4—H2N4 | 109.0 (13) | S1—C5—H5B | 109.5 |
| N3—C1—N1 | 115.96 (7) | H5A—C5—H5B | 109.5 |
| N3—C1—C2 | 123.34 (8) | S1—C5—H5C | 109.5 |
| N1—C1—C2 | 120.70 (7) | H5A—C5—H5C | 109.5 |
| C3—C2—C1 | 116.54 (8) | H5B—C5—H5C | 109.5 |
| C3—C2—H2A | 121.7 | | |

| | | | |
|-------------|-------------|-------------|-------------|
| N4—N3—C1—N1 | 176.97 (8) | C1—C2—C3—N2 | -0.32 (13) |
| N4—N3—C1—C2 | -4.05 (13) | C3—N2—C4—N1 | -0.91 (12) |
| C4—N1—C1—N3 | 179.94 (8) | C3—N2—C4—S1 | -179.53 (6) |
| C4—N1—C1—C2 | 0.92 (12) | C1—N1—C4—N2 | -0.07 (13) |
| N3—C1—C2—C3 | -179.68 (8) | C1—N1—C4—S1 | 178.65 (6) |
| N1—C1—C2—C3 | -0.74 (12) | C5—S1—C4—N2 | -12.16 (8) |
| C4—N2—C3—C2 | 1.08 (12) | C5—S1—C4—N1 | 169.01 (6) |

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|-----------------------------|------------|--------------|--------------|----------------|
| N3—H1N3...N1 ⁱ | 0.84 (2) | 2.24 (2) | 3.070 (1) | 172 (1) |
| N4—H1N4...N2 ⁱⁱ | 0.82 (2) | 2.42 (2) | 3.208 (1) | 161 (1) |
| N4—H2N4...N2 ⁱⁱⁱ | 0.89 (1) | 2.30 (2) | 3.137 (1) | 157 (1) |

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