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1-Vinyl-4-imidazoline-2-thione

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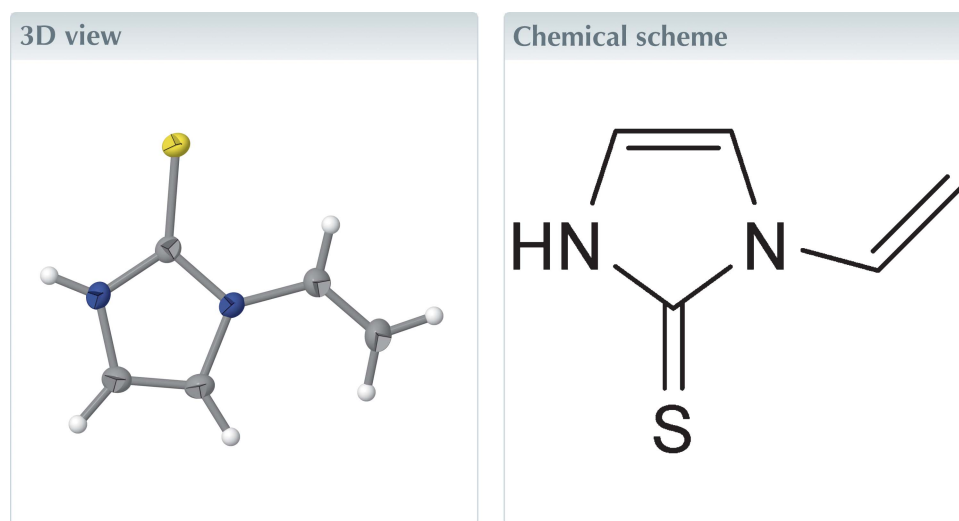
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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_5H_6N_2S$, was obtained by deprotonation of 1-vinylimidazole and subsequent reaction with elemental sulfur. In the crystal, the molecules are linked by $N-H \cdots S$ and $C-H \cdots S$ hydrogen bonds, and arranged in layers parallel to the *ab* plane.



Structure description

Imidazoline-2-thiones (Laus *et al.*, 2013) are versatile and easy-to-synthesize building blocks. The title compound is one of the small molecules whose structure, surprisingly, has not yet been described. Not only is the molecule itself interesting, it also allows further derivatization at the S and N atoms (Hummel *et al.*, 2017; Oberparleiter *et al.*, 2016), and gives access to a plethora of functionalized imidazolium salts. The primary alkylation takes place at the S atom; the resulting salt can then be deprotonated to yield a neutral 2-alkylsulfanyl-1-vinylimidazole, which can then be transformed into a quaternary salt. In addition, the vinyl substituent renders the molecule polymerizable and thus permits a path to imidazole-based polymers (Anderson & Long, 2010; Nakabayashi & Mori, 2013).

The synthesis of the title compound involves deprotonation of 1-vinylimidazole and subsequent reaction with elemental sulfur. Strong bases, such as isopropylmagnesium chloride or hexyllithium, are required. Other reaction conditions, such as sulfur in KOH/DMSO (Yuan *et al.*, 2010), $K_2CO_3/MeOH$ (Ansell *et al.*, 1970) or Et_3N /pyridine (Becker *et al.*, 1973), did not yield the desired product.

The $C=S$ bond length of 1.688 (1) Å is in agreement with the accepted value of 1.68 ± 0.02 Å for imidazoline-2-thiones (Laus *et al.*, 2013), ruling out the possibility of a thiol tautomer. The molecular structure is depicted in Fig. 1. The imidazoline-2-thione molecules are linked by $N-H \cdots S$ and $C-H \cdots S$ hydrogen bonds (Table 1) to form layers, which are arranged parallel to the *ab* plane (Fig. 2).

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots S1^i$	0.86 (1)	2.54 (1)	3.378 (1)	167 (1)
$C2-H2\cdots S1^{ii}$	0.95	2.82	3.728 (1)	160

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

Related structures, such as 3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazole-2-thione (Partl, Laus, Gelbrich *et al.*, 2017) and 3,3'-(hexane-1,6-diyl)bis(1-vinylimidazole-2-thione) (Partl, Laus, Kahlenberg *et al.*, 2017), have been reported recently. Polymorphs of the analogous 1-methylimidazole-2-thione ('methimazole') have been described (Lodochnikova *et al.*, 2013).

Synthesis and crystallization

Method A: isopropylmagnesium chloride solution (10 ml, 2 *M* in Et₂O, 20.0 mmol) was added to a solution of 1-vinylimidazole (1.52 g, 16.1 mmol) in anhydrous tetrahydrofuran (THF; 15 ml), and the mixture was stirred for 17 h under an argon atmosphere. Elemental sulfur (573 mg, 17.9 mmol) was added to the clear solution and stirring was continued at room temperature. After 28 h, H₂O (20 ml) was added and acidified with HCl (30 ml, 1 *M*, 30.0 mmol). The mixture was extracted with chloroform (3 × 40 ml). The combined organic phases were washed with H₂O (2 × 60 ml). The solvent was removed under reduced pressure, yielding 1.43 g (70%) of 1-vinylimidazole-2-thione as an off-white solid.

Method B: *n*-hexyllithium (16 ml, 2.3 *M* in hexanes, 36.8 mmol) was added to a cooled (193 K) solution of 1-vinylimidazole (3.07 g, 32.6 mmol) in anhydrous THF (40 ml) under an argon atmosphere. The mixture was stirred for 2 h at 195 K and then for 1 h at 263 K. Sulfur (1.1 g, 34.2 mmol) was added and stirring was continued for 68 h. The reaction was quenched with H₂O (20 ml) and acidified with

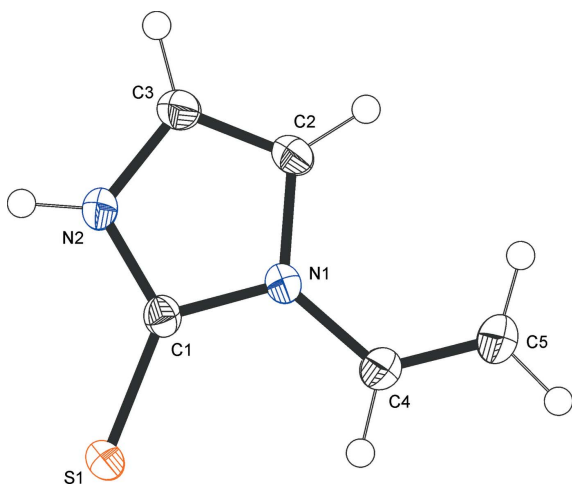


Figure 1
The molecular structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for the non-H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₅ H ₆ N ₂ S
M_r	126.18
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
a, b, c (Å)	10.7775 (3), 9.6848 (3), 12.1792 (4)
β (°)	108.139 (1)
V (Å ³)	1208.06 (6)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.42
Crystal size (mm)	0.17 × 0.12 × 0.07
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
T_{\min}, T_{\max}	0.864, 0.911
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16916, 1187, 1114
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.065, 1.08
No. of reflections	1187
No. of parameters	78
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.24, -0.22

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *XT* in *SHELXTL* (Bruker, 2014), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

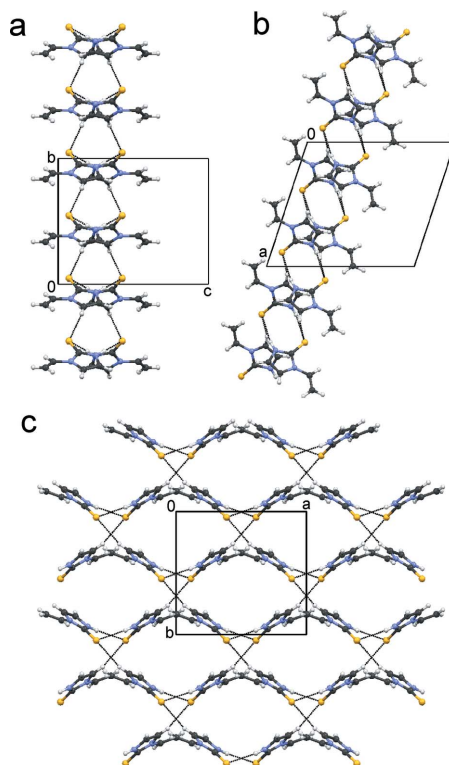


Figure 2
The unit cell of the title compound, viewed in the direction of (a) the *a* axis, (b) the *b* axis and (c) the *c* axis.

HCl (51 ml, 1 M, 51.0 mmol). The THF was removed under reduced pressure, and the residue was extracted with CHCl_3 (3×100 ml) and with EtOAc (100 ml). The combined organic phases were washed with H_2O (100 ml). The solution was treated with activated charcoal, followed by filtration over celite. The solvent was removed under reduced pressure and the product dried overnight at high vacuum, yielding 2.2 g (54%) of 1-vinylimidazole-2-thione as an off-white solid. Single crystals were obtained by slow evaporation of a solution in CHCl_3 (m.p. 416–418 K; sublimation above 396 K). The PXRD (Mo $K\alpha$ radiation) of the bulk material was an excellent match to that calculated from the single-crystal diffraction data (Fig. 3), indicating phase purity.

^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 12.35 (s, 1H), 7.52 (t, $J = 2.1$ Hz, 1H), 7.38 (dd, $J = 16.1, 9.1$ Hz, 1H), 7.04 (t, $J = 2.6$ Hz, 1H), 5.43 (dd, $J = 16.2, 1.3$ Hz, 1H), 4.92 (dd, $J = 9.1, 1.4$ Hz, 1H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 161.8, 129.0, 116.3, 113.8, 101.0. IR (neat): ν 3120, 3108, 3006, 1646, 1568, 1462, 1414, 1285, 1267, 1244, 1122, 1090, 1022, 960, 875, 772, 742, 682, 651, 545, 491 cm^{-1} .

Refinement

The H atom at N2 was found and refined isotropically with an N–H bond-length restraint of 0.87 (2) Å. Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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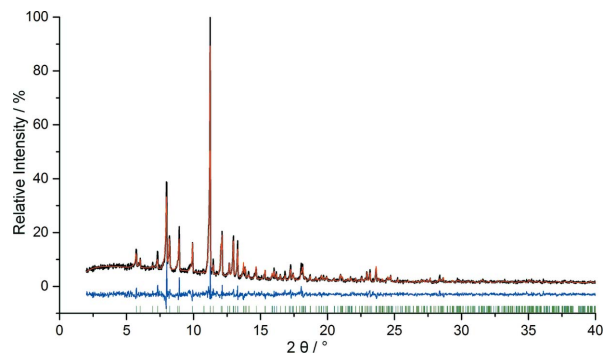


Figure 3

Rietveld fit ($R_{\text{wp}} = 0.126$, $R_{\text{exp}} = 0.121$, $R_p = 0.096$, goodness-of-fit = 1.04) of the PXRD data with a model calculated from the structural data of the single-crystal structure determination. Black dots indicate raw data, while the red line indicates the calculated model. Tick marks (green) are the hkl positions for the reflections. The difference curve is shown in blue.

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full crystallographic data

IUCrData (2017). **2**, x171207 [https://doi.org/10.1107/S241431461701207X]

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Crystal data

$C_5H_6N_2S$

$M_r = 126.18$

Monoclinic, $C2/c$

$a = 10.7775$ (3) Å

$b = 9.6848$ (3) Å

$c = 12.1792$ (4) Å

$\beta = 108.139$ (1)°

$V = 1208.06$ (6) Å³

$Z = 8$

$F(000) = 528$

$D_x = 1.387$ Mg m⁻³

Melting point: 418 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9910 reflections

$\theta = 2.9$ – 26.4 °

$\mu = 0.42$ mm⁻¹

$T = 173$ K

Prism, colourless

$0.17 \times 0.12 \times 0.07$ mm

Data collection

Bruker D8 QUEST PHOTON 100
diffractometer

Radiation source: Incoatec Microfocus

Multi layered optics monochromator

Detector resolution: 10.4 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

$T_{\min} = 0.864$, $T_{\max} = 0.911$

16916 measured reflections

1187 independent reflections

1114 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.9$ °

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.065$

$S = 1.08$

1187 reflections

78 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 1.0869P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0068 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atom at N2 were found and refined isotropically with bond restraint (d=87pm).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.11344 (3)	0.54728 (4)	0.42718 (3)	0.02539 (14)
N1	0.31623 (10)	0.38500 (11)	0.41324 (9)	0.0200 (2)
N2	0.17797 (11)	0.43417 (12)	0.24678 (9)	0.0225 (2)
H2N	0.1110 (15)	0.4659 (17)	0.1942 (13)	0.034 (4)*
C1	0.20309 (12)	0.45566 (12)	0.36118 (11)	0.0192 (3)
C2	0.35897 (13)	0.32017 (14)	0.32890 (11)	0.0241 (3)
H2	0.4349	0.2647	0.3421	0.029*
C3	0.27288 (13)	0.35079 (14)	0.22622 (11)	0.0250 (3)
H3	0.2762	0.3209	0.1529	0.030*
C4	0.37875 (13)	0.38285 (14)	0.53361 (11)	0.0262 (3)
H4	0.3320	0.4176	0.5821	0.031*
C5	0.49716 (14)	0.33608 (16)	0.58291 (12)	0.0327 (3)
H5A	0.5466	0.3006	0.5369	0.039*
H5B	0.5335	0.3376	0.6647	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01913 (19)	0.0318 (2)	0.0239 (2)	0.00659 (12)	0.00469 (13)	-0.00509 (12)
N1	0.0173 (5)	0.0214 (5)	0.0203 (5)	0.0030 (4)	0.0045 (4)	0.0000 (4)
N2	0.0179 (5)	0.0267 (6)	0.0197 (5)	0.0030 (4)	0.0014 (4)	-0.0020 (4)
C1	0.0159 (6)	0.0192 (6)	0.0213 (6)	-0.0016 (4)	0.0042 (5)	-0.0007 (4)
C2	0.0215 (6)	0.0253 (7)	0.0260 (7)	0.0045 (5)	0.0081 (5)	-0.0034 (5)
C3	0.0226 (6)	0.0280 (7)	0.0244 (7)	0.0015 (5)	0.0074 (5)	-0.0055 (5)
C4	0.0277 (7)	0.0303 (7)	0.0199 (6)	0.0060 (5)	0.0066 (5)	0.0020 (5)
C5	0.0319 (8)	0.0397 (8)	0.0227 (7)	0.0104 (6)	0.0028 (6)	0.0026 (6)

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

S1—C1	1.6884 (13)	C2—C3	1.3380 (19)
N1—C1	1.3695 (16)	C2—H2	0.9500
N1—C2	1.3986 (16)	C3—H3	0.9500
N1—C4	1.4102 (16)	C4—C5	1.3104 (19)
N2—C1	1.3502 (16)	C4—H4	0.9500
N2—C3	1.3858 (17)	C5—H5A	0.9500
N2—H2N	0.859 (14)	C5—H5B	0.9500
C1—N1—C2	109.49 (10)	N1—C2—H2	126.4
C1—N1—C4	123.85 (11)	C2—C3—N2	107.24 (11)
C2—N1—C4	126.64 (11)	C2—C3—H3	126.4
C1—N2—C3	110.74 (11)	N2—C3—H3	126.4
C1—N2—H2N	124.5 (11)	C5—C4—N1	124.29 (13)
C3—N2—H2N	124.7 (11)	C5—C4—H4	117.9

N2—C1—N1	105.33 (11)	N1—C4—H4	117.9
N2—C1—S1	127.71 (10)	C4—C5—H5A	120.0
N1—C1—S1	126.95 (10)	C4—C5—H5B	120.0
C3—C2—N1	107.21 (11)	H5A—C5—H5B	120.0
C3—C2—H2	126.4		
C3—N2—C1—N1	0.31 (14)	C1—N1—C2—C3	-0.01 (15)
C3—N2—C1—S1	-178.63 (10)	C4—N1—C2—C3	-178.69 (12)
C2—N1—C1—N2	-0.18 (14)	N1—C2—C3—N2	0.19 (15)
C4—N1—C1—N2	178.55 (11)	C1—N2—C3—C2	-0.32 (15)
C2—N1—C1—S1	178.77 (10)	C1—N1—C4—C5	-167.81 (14)
C4—N1—C1—S1	-2.51 (18)	C2—N1—C4—C5	10.7 (2)

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—H2N \cdots S1 ⁱ	0.86 (1)	2.54 (1)	3.378 (1)	167 (1)
C2—H2 \cdots S1 ⁱⁱ	0.95	2.82	3.728 (1)	160

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