

(3,5-Dimethyl-1*H*-pyrazol-1-yl)trimethylsilane

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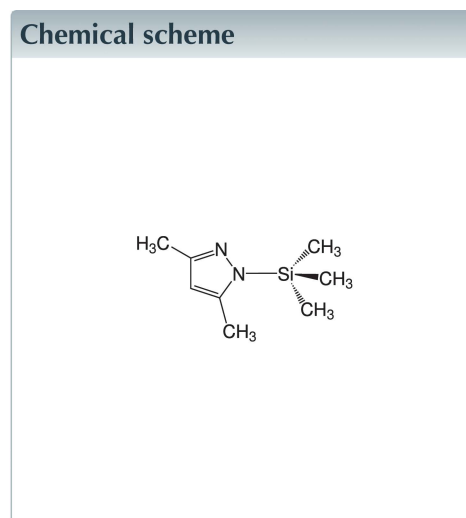
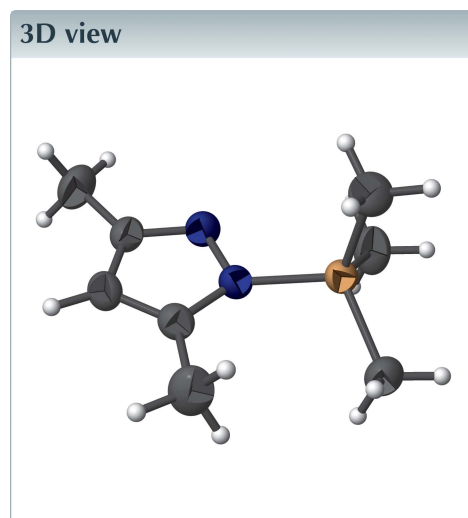
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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₈H₁₆N₂Si, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with one molecule in the asymmetric unit. The Si–N bond is 1.782 (2) Å, which is substantially longer than is found in comparable (3,5-dimethylpyrazolyl)silanes. The trimethylsilyl group adopts a staggered conformation with respect to the planar 3,5-dimethylpyrazolyl unit. C–H···N hydrogen bonds between neighboring molecules form a strand of molecules along the *b*-axis direction.



Structure description

Silanes substituted with 3,5-dimethylpyrazolyl units have been investigated over the last twenty years as an alternative to the long-known pyrazolylborates (Pullen *et al.*, 2000; Kuzu *et al.*, 2008; Armbruster *et al.* 2009). Such (3,5-dimethylpyrazolyl)silanes form potent multidentate ligands with a ‘podand topology’ (Gade 2002*a,b,c*).

The title compound (3,5-dimethyl-1*H*-pyrazol-1-yl)trimethylsilane is a key compound in the preparation of different (3,5-dimethylpyrazolyl)silanes by transsilylation (Armbruster *et al.*, 2009; Bitto *et al.*, 2012, 2013, 2016*a*). The solid-state structure of this compound has never been determined, since it is a liquid at room temperature. *In situ* cryo-crystallization of low-melting compounds has been practiced for many years (Atoji *et al.*, 1955; Smith & Lipscomb, 1965; Brodalla *et al.*, 1985). Different *in situ* cryo-crystallization techniques have been described in a review (Boese & Nussbaumer, 1994). State of the art of *in situ* crystallization is summarized recently in a special issue of *Zeitschrift für Kristallographie* (Boese, 2014). We have performed several single-crystal structure determinations of pyrophoric liquids by *in situ* crystallization on the diffractometer (Schmidt *et al.*, 2013; Gerwig *et al.* 2020). With the experience gained in these processes, we were able to crystallize the title compound on the diffractometer and we report its crystal structure here.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C6-H6B\cdots N2^i$	0.97	2.75	3.670 (3)	159

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

The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit (Fig. 1). The Si1–N1 bond is 1.782 (2) Å long. This is substantially longer than comparable bonds in tris(3,5-dimethylpyrazolyl)methylsilane [1.745 (5) Å; Vepachedu *et al.*, 1995] and tetrakis(3,5-dimethylpyrazolyl)silane [from 1.712 (3) to 1.725 (3) Å; Armbruster *et al.* 2009]. The pyrazol ring is planar with an r.m.s. deviation of 0.003 Å from the ring plane. The trimethylsilyl group adopts a staggered conformation with respect to the plane of the 3,5-dimethylpyrazolyl unit. This can be seen in the torsion angles C8–Si1–N1–N2 with $-35.1 (2)^\circ$ and C6–Si1–N1–C2 with $36.3 (2)^\circ$. The methyl group C7 is orientated perpendicular to the 3,5-dimethylpyrazolyl unit. There is a hydrogen bond between the hydrogen atom at C6 and the nitrogen atom N2 from a neighboring molecule (see Table 1). These hydrogen bonds form a strand of molecules generated by a twofold screw axis (2_1) along the crystallographic b axis (see Fig. 2).

Synthesis and crystallization

The title compound was prepared from 3,5-dimethylpyrazol (19.23 g, 0.2 mol) and chlorotrimethylsilane (22.81 g, 0.21 mol). The reaction was performed in 300 ml THF as solvent and in the presence of triethylamine (21.25 g, 0.21 mol). Triethylamine hydrochloride is formed during the reaction as a voluminous white precipitate. This precipitate is filtered off. After that the solvent is distilled off *in vacuo*. The

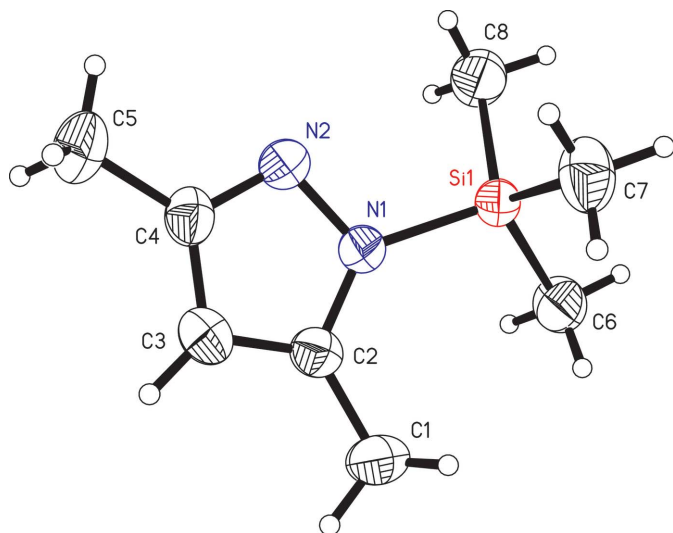


Figure 1
The molecular structure of the title compound, drawn with 50% probability displacement ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{16}N_2Si$
M_r	168.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	250
a, b, c (Å)	6.1056 (3), 10.8114 (7), 15.5867 (9)
V (Å ³)	1028.88 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.18
Crystal size (mm)	0.50 × 0.40 × 0.40
Data collection	
Diffractometer	STOE <i>IPDS 2</i>
Absorption correction	Integration (<i>X-RED</i> ; Stoe, 2009)
T_{min}, T_{max}	0.708, 0.932
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8249, 2346, 2258
R_{int}	0.048
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.080, 1.09
No. of reflections	2346
No. of parameters	106
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.12, -0.15
Absolute structure	Flack x determined using 896 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.07 (9)

Computer programs: *X-AREA* and *X-RED* (Stoe, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

title compound is isolated by vacuum distillation at 107°C and 1.3 kPa. It is a colourless liquid (26.97 g, 0.16 mol, 80% yield) (Bitto 2016b).

The compound was filled as liquid with 10% *n*-pentane in a glass capillary with 0.5 mm diameter. A single crystal was grown on the diffractometer at 255 K. The data collection was performed at a slightly lower temperature in order to have a stable crystal on the diffractometer.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

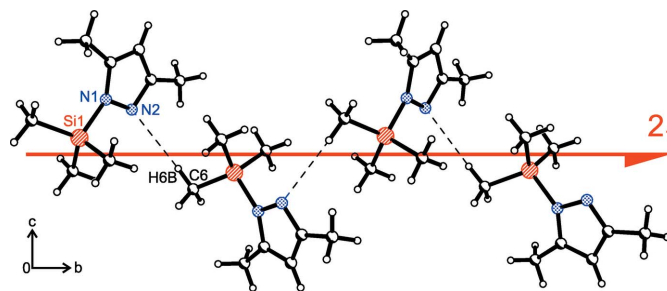


Figure 2
Hydrogen bonds between N2 and H6B of neighboring molecules along a twofold screw axis (2_1) parallel to the crystallographic b axis.

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full crystallographic data

IUCrData (2020). 5, x201444 [https://doi.org/10.1107/S2414314620014443]

(3,5-Dimethyl-1*H*-pyrazol-1-yl)trimethylsilane

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(3,5-Dimethyl-1*H*-pyrazol-1-yl)trimethylsilane*Crystal data*

$C_8H_{16}N_2Si$

$M_r = 168.32$

Orthorhombic, $P2_12_12_1$

$a = 6.1056$ (3) Å

$b = 10.8114$ (7) Å

$c = 15.5867$ (9) Å

$V = 1028.88$ (10) Å³

$Z = 4$

$F(000) = 368$

$D_x = 1.087$ Mg m⁻³

Melting point: 260 K

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

Cell parameters from 32385 reflections

$\theta = 2.3$ – 29.7°

$\mu = 0.18$ mm⁻¹

$T = 250$ K

Capillary, colourless

$0.50 \times 0.40 \times 0.40$ mm

Data collection

STOE IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration (X-RED; Stoe, 2009)

$T_{\min} = 0.708$, $T_{\max} = 0.932$

8249 measured reflections

2346 independent reflections

2258 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -7 \rightarrow 6$

$k = -14 \rightarrow 14$

$l = -19 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.080$

$S = 1.09$

2346 reflections

106 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 0.1226P]$

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

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

$\Delta\rho_{\max} = 0.12$ e Å⁻³

$\Delta\rho_{\min} = -0.15$ e Å⁻³

Extinction correction: SHELXL-2014/7

(Sheldrick 2015,

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

Extinction coefficient: 0.038 (8)

Absolute structure: Flack x determined using 896 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.07 (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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	1.09038 (8)	0.83129 (5)	0.28856 (3)	0.03560 (16)
N1	0.9829 (3)	0.91025 (15)	0.37963 (9)	0.0371 (3)
N2	0.8044 (3)	0.98582 (17)	0.36345 (11)	0.0449 (4)
C1	1.2467 (4)	0.8620 (3)	0.49915 (16)	0.0604 (6)
H1A	1.2704	0.8905	0.5574	0.091*
H1B	1.3765	0.8782	0.4651	0.091*
H1C	1.2171	0.7738	0.4996	0.091*
C2	1.0558 (3)	0.92883 (18)	0.46120 (11)	0.0390 (4)
C3	0.9227 (4)	1.01575 (19)	0.49782 (12)	0.0443 (4)
H3	0.9317	1.0469	0.5540	0.053*
C4	0.7709 (4)	1.04880 (18)	0.43507 (13)	0.0422 (4)
C5	0.5894 (5)	1.1411 (2)	0.44085 (18)	0.0670 (7)
H5A	0.6504	1.2230	0.4493	0.100*
H5B	0.4951	1.1204	0.4888	0.100*
H5C	0.5049	1.1397	0.3882	0.100*
C6	1.2361 (4)	0.6905 (2)	0.32373 (15)	0.0544 (6)
H6A	1.3721	0.7136	0.3516	0.082*
H6B	1.2677	0.6390	0.2743	0.082*
H6C	1.1450	0.6449	0.3637	0.082*
C7	1.2781 (5)	0.9387 (2)	0.23290 (16)	0.0593 (6)
H7A	1.1987	1.0127	0.2163	0.089*
H7B	1.3368	0.8989	0.1821	0.089*
H7C	1.3972	0.9610	0.2711	0.089*
C8	0.8569 (4)	0.7920 (3)	0.21896 (16)	0.0589 (6)
H8A	0.7518	0.7433	0.2511	0.088*
H8B	0.9084	0.7447	0.1701	0.088*
H8C	0.7875	0.8675	0.1990	0.088*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0353 (2)	0.0376 (3)	0.0339 (2)	0.0038 (2)	0.0023 (2)	0.00083 (19)
N1	0.0377 (8)	0.0398 (8)	0.0338 (7)	0.0062 (7)	0.0010 (6)	0.0016 (6)
N2	0.0477 (10)	0.0474 (9)	0.0395 (8)	0.0141 (8)	-0.0014 (7)	0.0014 (7)
C1	0.0550 (13)	0.0720 (16)	0.0541 (13)	0.0143 (12)	-0.0176 (10)	-0.0073 (11)
C2	0.0396 (10)	0.0414 (9)	0.0361 (8)	-0.0028 (8)	-0.0016 (8)	0.0000 (7)
C3	0.0515 (11)	0.0435 (10)	0.0380 (8)	-0.0020 (10)	0.0016 (9)	-0.0049 (8)
C4	0.0452 (11)	0.0375 (10)	0.0438 (10)	0.0042 (8)	0.0072 (8)	-0.0007 (7)
C5	0.0701 (16)	0.0590 (14)	0.0718 (16)	0.0264 (14)	0.0064 (14)	-0.0074 (11)

C6	0.0651 (14)	0.0476 (12)	0.0506 (12)	0.0175 (11)	0.0024 (11)	0.0007 (9)
C7	0.0599 (14)	0.0557 (13)	0.0623 (14)	-0.0014 (12)	0.0219 (12)	0.0060 (10)
C8	0.0500 (12)	0.0713 (15)	0.0554 (13)	0.0044 (11)	-0.0075 (10)	-0.0176 (12)

Geometric parameters (Å, °)

Si1—N1	1.7816 (15)	C4—C5	1.494 (3)
Si1—C8	1.841 (2)	C5—H5A	0.9700
Si1—C6	1.847 (2)	C5—H5B	0.9700
Si1—C7	1.848 (2)	C5—H5C	0.9700
N1—C2	1.362 (2)	C6—H6A	0.9700
N1—N2	1.385 (2)	C6—H6B	0.9700
N2—C4	1.324 (3)	C6—H6C	0.9700
C1—C2	1.494 (3)	C7—H7A	0.9700
C1—H1A	0.9700	C7—H7B	0.9700
C1—H1B	0.9700	C7—H7C	0.9700
C1—H1C	0.9700	C8—H8A	0.9700
C2—C3	1.367 (3)	C8—H8B	0.9700
C3—C4	1.394 (3)	C8—H8C	0.9700
C3—H3	0.9400		
N1—Si1—C8	107.15 (10)	C4—C5—H5A	109.5
N1—Si1—C6	109.63 (9)	C4—C5—H5B	109.5
C8—Si1—C6	110.98 (13)	H5A—C5—H5B	109.5
N1—Si1—C7	107.53 (10)	C4—C5—H5C	109.5
C8—Si1—C7	110.39 (13)	H5A—C5—H5C	109.5
C6—Si1—C7	111.02 (13)	H5B—C5—H5C	109.5
C2—N1—N2	109.87 (15)	Si1—C6—H6A	109.5
C2—N1—Si1	133.98 (14)	Si1—C6—H6B	109.5
N2—N1—Si1	115.29 (11)	H6A—C6—H6B	109.5
C4—N2—N1	105.74 (16)	Si1—C6—H6C	109.5
C2—C1—H1A	109.5	H6A—C6—H6C	109.5
C2—C1—H1B	109.5	H6B—C6—H6C	109.5
H1A—C1—H1B	109.5	Si1—C7—H7A	109.5
C2—C1—H1C	109.5	Si1—C7—H7B	109.5
H1A—C1—H1C	109.5	H7A—C7—H7B	109.5
H1B—C1—H1C	109.5	Si1—C7—H7C	109.5
N1—C2—C3	107.29 (18)	H7A—C7—H7C	109.5
N1—C2—C1	123.58 (18)	H7B—C7—H7C	109.5
C3—C2—C1	129.12 (19)	Si1—C8—H8A	109.5
C2—C3—C4	106.16 (17)	Si1—C8—H8B	109.5
C2—C3—H3	126.9	H8A—C8—H8B	109.5
C4—C3—H3	126.9	Si1—C8—H8C	109.5
N2—C4—C3	110.94 (18)	H8A—C8—H8C	109.5
N2—C4—C5	120.6 (2)	H8B—C8—H8C	109.5
C3—C4—C5	128.5 (2)		
C8—Si1—N1—C2	156.8 (2)	Si1—N1—C2—C3	169.00 (16)

C6—Si1—N1—C2	36.3 (2)	N2—N1—C2—C1	-179.88 (19)
C7—Si1—N1—C2	-84.5 (2)	Si1—N1—C2—C1	-11.4 (3)
C8—Si1—N1—N2	-35.13 (18)	N1—C2—C3—C4	-0.7 (2)
C6—Si1—N1—N2	-155.65 (15)	C1—C2—C3—C4	179.8 (2)
C7—Si1—N1—N2	83.55 (17)	N1—N2—C4—C3	-0.3 (2)
C2—N1—N2—C4	-0.1 (2)	N1—N2—C4—C5	179.69 (19)
Si1—N1—N2—C4	-171.00 (14)	C2—C3—C4—N2	0.6 (3)
N2—N1—C2—C3	0.5 (2)	C2—C3—C4—C5	-179.4 (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>
C6—H6B \cdots N2 ⁱ	0.97	2.75	3.670 (3)	159

Symmetry code: (i) $-x+2, y-1/2, -z+1/2$.