



Crystal structure of 3-methyl-5-trimethylsilyl-1*H*-pyrazole

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Received 30 April 2015; accepted 1 May 2015

Edited by M. Zeller, Youngstown State University, USA

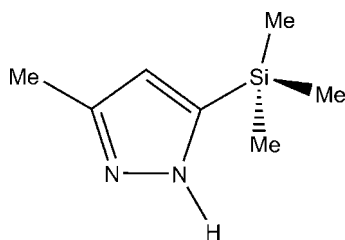
The title compound, C₇H₁₄N₂Si, crystallizes in a tetragonal space group and exists as an N—H···N hydrogen-bonded tetramer, formed around the crystallographic fourfold roto-inversion axis. The molecular identity is clearly the 5-trimethylsilyl-3-methyl-1*H*-pyrazole tautomer and the structure is isomorphous with that of 5-*tert*-butyl-3-methyl-1*H*-pyrazole [Foces-Foces & Trofimenko (2001). *Acta Cryst. E* **57**, o32–o34].

Keywords: crystal structure; pyrazole; tetramer; hydrogen bonding.

CCDC reference: 1062812

1. Related literature

For synthetic preparation of the title compound, see: Aoyama *et al.* (1984). For isomorphous 5-*tert*-butyl-3-methyl-1*H*-pyrazole, see: Foces-Foces & Trofimenko (2001). For a general introduction to polypyrazolylborate chemistry, see: Trofimenko (1999). For related structures, see the Cambridge Structural Database: Groom & Allen (2014).



2. Experimental

2.1. Crystal data

C₇H₁₄N₂Si
M_r = 154.29
Tetragonal, I₄/a
a = 19.221 (3) Å

c = 10.5812 (18) Å
V = 3909.4 (15) Å³
Z = 16
Mo Kα radiation

μ = 0.18 mm⁻¹
T = 100 K

0.3 × 0.22 × 0.09 mm

2.2. Data collection

Bruker SMART APEX CCD
diffractometer
Absorption correction: multi-scan
(APEX; Bruker, 2008)
T_{min} = 0.500, T_{max} = 0.746

14542 measured reflections
2240 independent reflections
1811 reflections with I > 2σ(I)
R_{int} = 0.046

2.3. Refinement

R[F² > 2σ(F²)] = 0.046
wR(F²) = 0.121
S = 1.11
2240 reflections
100 parameters

H atoms treated by a mixture of
independent and constrained
refinement
Δρ_{max} = 0.38 e Å⁻³
Δρ_{min} = -0.28 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2 ⁱ	0.87 (3)	2.03 (3)	2.895 (2)	171 (2)

Symmetry code: (i) $-y + \frac{3}{4}, x + \frac{3}{4}, -z + \frac{3}{4}$.

Data collection: APEX2 (Bruker, 2008); cell refinement: APEX2 and SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: WinGX (Farrugia, 2012) and publCIF (Westrip, 2010).

Acknowledgements

The authors thank Youngstown State University Structure & Chemical Instrumentation Facility's Matthias Zeller for X-ray data collection. The diffractometer was funded by NSF (grant No. 0087210), Ohio Board of Regents (grant CAP-491), and YSU.

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2621).

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supporting information

Acta Cryst. (2015). E71, o397 [doi:10.1107/S2056989015008567]

Crystal structure of 3-methyl-5-trimethylsilyl-1*H*-pyrazole

Gregory M. Ferrence and Joshua L. Kocher

S1. Chemical context

Pyrazoles, particularly 3,5-disubstituted pyrazoles have found widespread use in the preparation of trispyrazolylborate salts. The trispyrazolylborates make excellent supporting ligands for stabilization of a wide range of metal-organic coordination compounds. Most often functioning as tridentate ligands, this class of molecules is often referred to as the scorpionates (Trofimenko, 1999). We have studied a variety of tris(3-*tert*-butyl-5-methyl)pyrazolylborate supported metal complexes and have found the 27 proton *tert*-butyl resonance in the ¹H NMR to often obscure important resonances from other aliphatic fragments. Replacing the *tert*-butyl group with a trimethylsilyl group would clear the standard aliphatic region of the NMR spectrum. During the course of our studies, we obtained X-ray quality crystals of the title compound which is reported herein.

S2. Structural commentary

The title compound (Fig. 1) is isomorphous with known 5-*tert*-butyl-3-methyl-1*H*-pyrazole (Foces-Foces & Trofimenko, 2001). Apart from substitution of the tertiary carbon atom in 5-*tert*-butyl-3-methyl-1*H*-pyrazole with a silicon atom in the title compound, the structural features are nearly indistinguishable. At 100 K, the title structure appeared to have well ordered trimethylsilyl groups, while the 240 K structure of 5-*tert*-butyl-3-methyl-1*H*-pyrazole displayed rotational disorder of the *tert*-butyl group.

S3. Supramolecular features

Like 5-*tert*-butyl-3-methyl-1*H*-pyrazole, the title compound's packing includes an R₄⁴(12) hydrogen-bonding motif (Fig. 2).

S4. Database survey

Pyrazoles are ubiquitous, particularly as building blocks for pyrazolylborate metal complexes. Restricting a Cambridge Structural Database (Version 5.36, last update February 2015; Groom & Allen, 2014) search to include only those pyrazoles comprised of C, H, N, P, O, S, F, Cl, Br, I and Si returned nearly 900 entries which included over 750 different pyrazole compounds. Of these, 25 structures are in tetragonal space groups. Nine of these structures display the same R₄⁴(12) hydrogen-bonding motif as the title compound. These include CSD refcode entries: AFAWEK, FAQTIA, GIRNEA, QAMQEA, QOFWUD, RIWDUX, TUHNEQ, UXOVAF, YESWUP. In all of these structures, including the title compound, a crystallographic 4-fold rotoinversion axis is at the center of the H-bonding motif.

S5. Synthesis and crystallization

Synthesis of the title compound was accomplished following a literature procedure involving reaction of trimethylsilyl-diazomethane with *n*-butyllithium, followed by reaction with the α , β -unsaturated methacrylonitrile (Aoyama *et al.*, 1984). X-ray quality crystals were obtained by slow evaporation of a chloroform solution of the title compound.

S6. Refinement

The pyrazole-H atom was located in a difference Fourier map and refined freely. All other H atoms were initially located in a difference Fourier map, but were included in the final refinement using the standard geometrically idealized positions and refined using the riding-model approximation ($C-H = 0.95$ and 0.98 Å for Ar-H and CH_3 ; $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic H atom and $U_{iso}(H) = 1.5U_{eq}(C)$) for methyl groups. The H atoms of the C6-methyl group were refined as orientationally disordered using the AFIX 127 command in SHELX2014 (Sheldrick, 2015), with refined occupancies of 0.58 (3) and 0.42 (3) for the two moieties, respectively.

Crystal data, data collection and structure refinement details are summarized in Table 1.

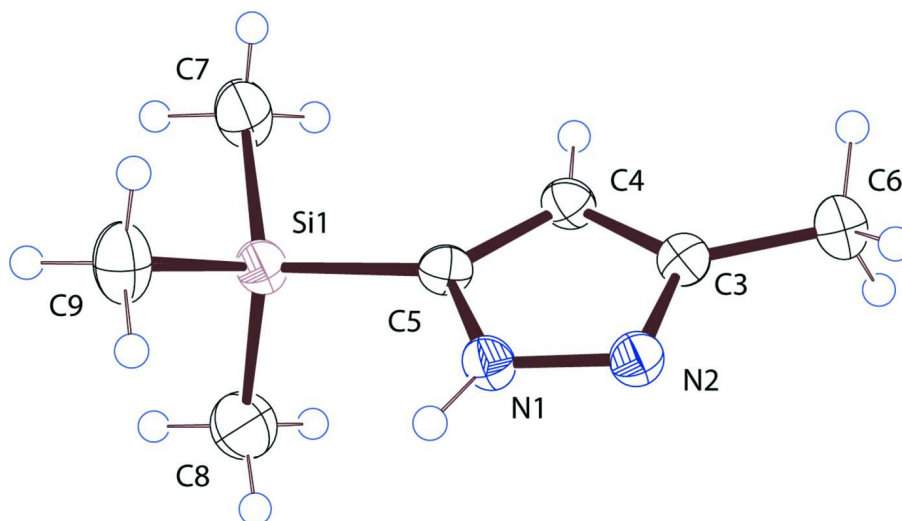
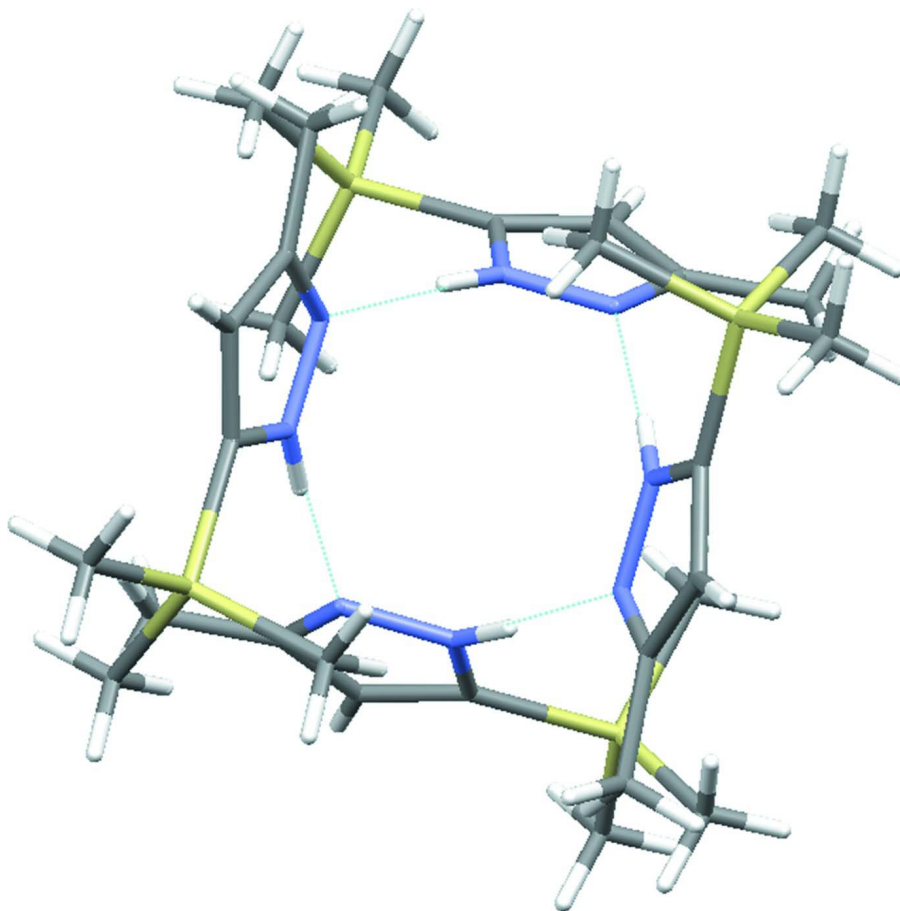


Figure 1

ORTEP-3 view of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Only the larger part of the disordered H-atoms attached to C6 are shown.

**Figure 2**

Mercury rendering of the $R_4^4(12)$ H-bonding motif view of the title compound.

3-Methyl-5-trimethylsilyl-1H-pyrazole

Crystal data

$C_7H_{14}N_2Si$

$M_r = 154.29$

Tetragonal, $I4_1/a$

Hall symbol: $-I\ 4ad$

$a = 19.221(3) \text{ \AA}$

$c = 10.5812(18) \text{ \AA}$

$V = 3909.4(15) \text{ \AA}^3$

$Z = 16$

$F(000) = 1344$

$D_x = 1.049 \text{ Mg m}^{-3}$

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

Cell parameters from 6620 reflections

$\theta = 2.2\text{--}31.0^\circ$

$\mu = 0.18 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Plate, colourless

$0.3 \times 0.22 \times 0.09 \text{ mm}$

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*APEX*; Bruker, 2008)

$T_{\min} = 0.500$, $T_{\max} = 0.746$

14542 measured reflections

2240 independent reflections

1811 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -24 \rightarrow 24$

$k = -24 \rightarrow 24$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.121$

$S = 1.11$

2240 reflections

100 parameters

0 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: iterative

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 6.7007P]$

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

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

$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Si1	0.15752 (3)	0.66265 (3)	0.08122 (5)	0.02652 (17)	
N2	-0.01542 (8)	0.63160 (8)	0.29098 (15)	0.0252 (3)	
N1	0.04990 (8)	0.65356 (8)	0.26486 (15)	0.0243 (3)	
C3	-0.03518 (10)	0.59551 (10)	0.18886 (18)	0.0242 (4)	
C4	0.01831 (10)	0.59437 (10)	0.09907 (17)	0.0252 (4)	
H4	0.0174	0.5719	0.0192	0.03*	
C5	0.07285 (10)	0.63252 (9)	0.14950 (17)	0.0233 (4)	
C7	0.17863 (12)	0.60908 (13)	-0.0598 (2)	0.0418 (6)	
H7A	0.2214	0.6265	-0.0989	0.063*	
H7B	0.1403	0.6119	-0.1207	0.063*	
H7C	0.1853	0.5605	-0.0341	0.063*	
C8	0.14560 (14)	0.75508 (12)	0.0363 (3)	0.0478 (6)	
H8A	0.1889	0.773	-0.0003	0.072*	
H8B	0.1336	0.7823	0.1115	0.072*	
H8C	0.1081	0.7588	-0.026	0.072*	
C6	-0.10613 (10)	0.56396 (11)	0.1820 (2)	0.0318 (5)	
H6A	-0.1042	0.521	0.1322	0.048*	0.58 (3)
H6B	-0.1382	0.5968	0.1416	0.048*	0.58 (3)
H6C	-0.1226	0.5534	0.2675	0.048*	0.58 (3)
H6D	-0.1391	0.5931	0.2287	0.048*	0.42 (3)
H6E	-0.1051	0.5173	0.2193	0.048*	0.42 (3)
H6F	-0.1207	0.5607	0.0934	0.048*	0.42 (3)
C9	0.22749 (12)	0.65443 (14)	0.2008 (2)	0.0422 (6)	
H9A	0.2322	0.6056	0.2259	0.063*	
H9B	0.2158	0.6826	0.2751	0.063*	
H9C	0.2715	0.6708	0.1648	0.063*	
H1	0.0738 (13)	0.6790 (13)	0.317 (2)	0.039 (7)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0269 (3)	0.0312 (3)	0.0214 (3)	-0.0041 (2)	0.0032 (2)	-0.0034 (2)
N2	0.0265 (8)	0.0282 (8)	0.0210 (8)	-0.0010 (6)	0.0025 (6)	-0.0018 (6)
N1	0.0265 (8)	0.0281 (8)	0.0182 (8)	-0.0038 (6)	0.0003 (6)	-0.0035 (6)
C3	0.0248 (9)	0.0251 (9)	0.0226 (9)	0.0008 (7)	-0.0015 (7)	0.0013 (7)
C4	0.0292 (9)	0.0265 (9)	0.0198 (9)	-0.0019 (7)	0.0000 (7)	-0.0043 (7)
C5	0.0278 (9)	0.0243 (9)	0.0178 (9)	0.0003 (7)	0.0013 (7)	-0.0007 (7)
C7	0.0378 (12)	0.0550 (14)	0.0327 (12)	-0.0121 (11)	0.0106 (9)	-0.0153 (10)
C8	0.0482 (14)	0.0380 (12)	0.0572 (16)	-0.0057 (10)	0.0120 (12)	0.0087 (11)
C6	0.0280 (10)	0.0350 (11)	0.0325 (11)	-0.0056 (8)	-0.0009 (8)	0.0010 (9)
C9	0.0326 (11)	0.0604 (15)	0.0336 (12)	-0.0079 (10)	-0.0020 (9)	0.0007 (11)

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

Si1—C8	1.853 (2)	C7—H7C	0.98
Si1—C9	1.854 (2)	C8—H8A	0.98
Si1—C7	1.858 (2)	C8—H8B	0.98
Si1—C5	1.8725 (19)	C8—H8C	0.98
N2—C3	1.339 (2)	C6—H6A	0.98
N2—N1	1.353 (2)	C6—H6B	0.98
N1—C5	1.359 (2)	C6—H6C	0.98
N1—H1	0.87 (3)	C6—H6D	0.98
C3—C4	1.400 (3)	C6—H6E	0.98
C3—C6	1.494 (3)	C6—H6F	0.98
C4—C5	1.386 (3)	C9—H9A	0.98
C4—H4	0.95	C9—H9B	0.98
C7—H7A	0.98	C9—H9C	0.98
C7—H7B	0.98		
C8—Si1—C9	110.27 (12)	H8A—C8—H8C	109.5
C8—Si1—C7	110.65 (13)	H8B—C8—H8C	109.5
C9—Si1—C7	110.04 (12)	C3—C6—H6A	109.5
C8—Si1—C5	106.74 (10)	C3—C6—H6B	109.5
C9—Si1—C5	109.92 (10)	H6A—C6—H6B	109.5
C7—Si1—C5	109.16 (9)	C3—C6—H6C	109.5
C3—N2—N1	105.07 (15)	H6A—C6—H6C	109.5
N2—N1—C5	113.06 (15)	H6B—C6—H6C	109.5
N2—N1—H1	122.3 (16)	C3—C6—H6D	109.5
C5—N1—H1	124.6 (16)	H6A—C6—H6D	141.1
N2—C3—C4	110.33 (16)	H6B—C6—H6D	56.3
N2—C3—C6	120.56 (17)	H6C—C6—H6D	56.3
C4—C3—C6	129.10 (18)	C3—C6—H6E	109.5
C5—C4—C3	106.61 (16)	H6A—C6—H6E	56.3
C5—C4—H4	126.7	H6B—C6—H6E	141.1
C3—C4—H4	126.7	H6C—C6—H6E	56.3
N1—C5—C4	104.93 (16)	H6D—C6—H6E	109.5

N1—C5—Si1	122.45 (14)	C3—C6—H6F	109.5
C4—C5—Si1	132.25 (14)	H6A—C6—H6F	56.3
Si1—C7—H7A	109.5	H6B—C6—H6F	56.3
Si1—C7—H7B	109.5	H6C—C6—H6F	141.1
H7A—C7—H7B	109.5	H6D—C6—H6F	109.5
Si1—C7—H7C	109.5	H6E—C6—H6F	109.5
H7A—C7—H7C	109.5	Si1—C9—H9A	109.5
H7B—C7—H7C	109.5	Si1—C9—H9B	109.5
Si1—C8—H8A	109.5	H9A—C9—H9B	109.5
Si1—C8—H8B	109.5	Si1—C9—H9C	109.5
H8A—C8—H8B	109.5	H9A—C9—H9C	109.5
Si1—C8—H8C	109.5	H9B—C9—H9C	109.5
<hr/>			
C3—N2—N1—C5	-0.2 (2)	C3—C4—C5—Si1	-172.39 (15)
N1—N2—C3—C4	0.6 (2)	C8—Si1—C5—N1	-72.00 (19)
N1—N2—C3—C6	-178.76 (17)	C9—Si1—C5—N1	47.58 (19)
N2—C3—C4—C5	-0.7 (2)	C7—Si1—C5—N1	168.37 (16)
C6—C3—C4—C5	178.57 (19)	C8—Si1—C5—C4	99.9 (2)
N2—N1—C5—C4	-0.2 (2)	C9—Si1—C5—C4	-140.6 (2)
N2—N1—C5—Si1	173.60 (13)	C7—Si1—C5—C4	-19.8 (2)
C3—C4—C5—N1	0.5 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...N2 ⁱ	0.87 (3)	2.03 (3)	2.895 (2)	171 (2)

Symmetry code: (i) $-y+3/4, x+3/4, -z+3/4$.