| | | | |
|---|---|---|---|
| C(1)—C(2)—C(3) | 114.7 (5) | O(1)—P(1)—O(4) | 109.1 (3) |
| C(2)—C(3)—C(4) | 113.8 (4) | O(2)—P(1)—O(4) | 108.0 (4) |
| C(3)—C(4)—C(5) | 114.5 (4) | O(3)—P(1)—O(4) | 109.7 (4) |
| C(4)—C(5)—C(6) | 114.4 (4) | O(1)—P(1)—O(31) | 112.9 (3) |
| C(5)—C(6)—C(7) | 115.0 (4) | O(1)—P(1)—O(41) | 109.6 (3) |
| C(6)—C(7)—C(8) | 112.5 (4) | O(1)—P(1)—O(21) | 104.2 (3) |
| N—C(8)—C(7) | 112.4 (4) | O(31)—P(1)—O(21) | 112.8 (4) |
| O(1)—P(1)—O(2) | 105.7 (3) | O(31)—P(1)—O(41) | 110.0 (4) |
| O(1)—P(1)—O(3) | 107.8 (3) | O(41)—P(1)—O(21) | 107.0 (4) |
| O(2)—P(1)—O(3) | 116.4 (4) | | |

Table 5. *Hydrogen bonds* (Å, °)

| N—H···O | H···O | N···O | N—H···O |
|---|---|---|---|
| C7ADP | | | |
| N—H(1)···O(2$^{i}$) | 2.242 (9) | 2.960 (11) | 146.0 (4) |
| N—H(1)···O(31$^{i}$) | 1.986 (7) | 2.805 (9) | 173.8 (3) |
| N—H(2)···O(4) | 1.932 (7) | 2.767 (8) | 153.8 (4) |
| N—H(2)···O(41) | 1.910 (7) | 2.774 (8) | 160.5 (4) |
| N—H(3)···O(21$^{ii}$) | 2.083 (10) | 2.964 (12) | 154.7 (3) |
| N—H(3)···O(3$^{ii}$) | 1.929 (8) | 2.861 (10) | 168.8 (4) |
| C8ADP | | | |
| N—H(1)···O(2$^{iii}$) | 1.944 (7) | 2.796 (9) | 158.1 (4) |
| N—H(1)···O(31$^{iii}$) | 2.079 (8) | 2.949 (10) | 163.5 (4) |
| N—H(2)···O(4$^{iv}$) | 1.926 (6) | 2.768 (8) | 160.4 (4) |
| N—H(2)···O(41$^{v}$) | 1.925 (6) | 2.765 (8) | 159.4 (4) |
| N—H(3)···O(21$^{v}$) | 2.117 (11) | 2.859 (8) | 172.3 (3) |
| N—H(3)···O(3$^{v}$) | 2.342 (12) | 2.984 (10) | 147.8 (5) |

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

The crystal quality, preliminary cell constants and diffraction symmetry were determined from Weissenberg photographs (systematic absences: $h0l$, $l = 2n + 1$; $0k0$; $k = 2n + 1$) and optical indicatrix observations under a polarizing microscope. The samples selected for the intensity-data collection were ground into spheres; because of their ferroelasticity this was performed using wet blotting paper.

The structures were solved by direct methods. *E* maps revealed the positions of the P atom, one well defined atom of the $H_2PO_4$ group [O(1)] and all the non-H atoms forming the *n*-alkylammonium chain. After a full-matrix least-squares refinement of these fragments, using isotropic displacement factors, the $\Delta\rho$ map showed six peaks of electron density $\sim$4 e Å$^{-3}$ within the P coordination sphere. The *z* coordinates for pairs of these peaks were mirror related. Assuming partial disorder of the $PO_4$ group, the peaks were assigned to the three missing O atoms and then refined with the position occupancy factor $K = 0.5$ (*R* factors were 0.078 and 0.086 for C7ADP and C8ADP, respectively). The final $\Delta\rho$ maps revealed most H atoms of the *n*-alkylammonium chains except for those belonging to the terminal methyl and ammonium groups, which were placed in calculated positions. In the last stages of the refinement, positional parameters of all H atoms were fixed and only their isotropic temperature coefficients were refined. The two acid protons could not be localized unambiguously and were not included in the calculations.

Data collection, cell refinement and data reduction: *KM*-4 (Kuma, 1992). Structure solution, refinement and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Preparation of material for publication: *SHELXTL/PC* and local programs.

AW thanks Dr A. Pietraszko for his assistance in using a Kuma KM-4 diffractometer, Professor Z. Gałdecki (Technical University of Łódź) for allowing the use of the Siemens *SHELXTL/PC* program system and Dr J. Zaleski for valuable discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB0326). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Tris(3,5-dimethylpyrazol-1-yl)methylsilane

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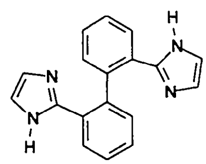
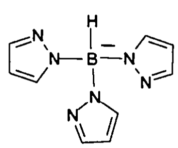
## Abstract

The structure consists of discrete molecules of tris(3,5-dimethylpyrazol-1-yl)methylsilane, $C_{16}H_{24}N_6Si$, that exhibit distorted tetrahedral SiN(pyrazole)$_3$C geometry about the Si atom. The Si and methyl C atoms lie on threefold axes. The C—Si—N and N—Si—N bond angles are 111.3 (2) and 107.5 (2)°, respectively, while the Si—N bond length is 1.745 (5) Å. The present work provides the first reported structure containing an Si—N(pyrazole) linkage.

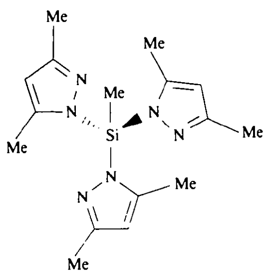
## Comment

As part of a long-term project designed to aid understanding of the structural and spectroscopic properties of the active sites of selected metalloproteins, we have prepared and characterized numerous low molecular weight analogues (Potenza, Stibrany, Potenza & Schugar, 1992). A particular challenge has been to prepare pseudo-tetrahedral or pseudo-$C_{3v}$ complexes with Cu$^{II}$, an ion whose ligand field strongly favors square-planar or tetragonal coordination geometries. The bidentate ligand 2,2′-bis(2-imidazolyl)biphenyl, (2), was found to impose steric constraints on $Cu^{II}$ and other metal ions to yield pseudo-tetrahedral $M^{II}N_4$ complexes (Knapp, Keenan, Zhang, Fikar, Potenza & Schugar, 1990). The sterically constraining tridentate ligand tris(pyrazolyl)borate, (3), has recently been used to construct pseudo-$C_{3v}$ $CuN_3S$ analogues of the type I copper metalloenzymes (Kitajima, Fujisawa, Tanaka & Moro-oka, 1992). A neutral analogue of (3), tris(pyrazol-1-yl)methane, (4), has been used to prepare tetragonal and distorted octahedral complexes $M(4)_2$, where (4) is $C_{10}H_{10}N_6$ (Astley, Gulbis, Hitchman & Tiekink, 1993). The relatively short B—N and C—N bonds in (3) and (4) (1.43–1.65 Å) enforce small cone angles in their metal complexes, leading to N—*M*—N angles substantially smaller than the tetrahedral angle. The goal in the present study was to prepare a neutral analogue of (3) with a longer pyrazole–bridgehead-atom bond length. It is hoped that the added bond length will increase the cone angle and yield metalloenzyme models with N—*M*—N angles closer to the ideal value. Tris(1-pyrazolyl)phosphine, (5), with a longer P—N bond length [1.714 (4) Å; Cobbledick & Einstein, 1975] also has the potential to increase the cone angle, but this compound is not oxidatively stable in the presence of $Cu^{II}$.


(2)


(3)

The title compound, (1), was prepared by a transsilylation technique used to prepare silylbenzimidazoles (Jutzi & Sakriss, 1973).


(1)

The structure consists of discrete molecules of (1) with no unusually short intermolecular contacts. In $P6_3$, the molecules utilize a crystallographic threefold axis (site *b*, $\frac{1}{3}$, $\frac{2}{3}$, *z*; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}+z$) and one-third of a molecule comprises the asymmetric unit. The pyrazole N atoms and a methyl C atom provide a

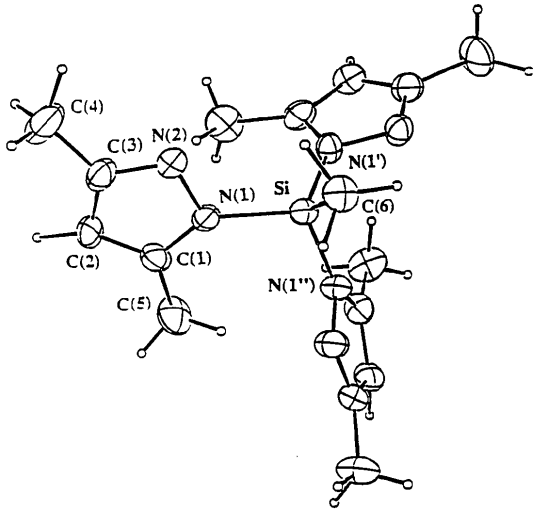


Fig. 1. View (*ORTEP*II; Johnson, 1976) of compound (1) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 33% probability level.

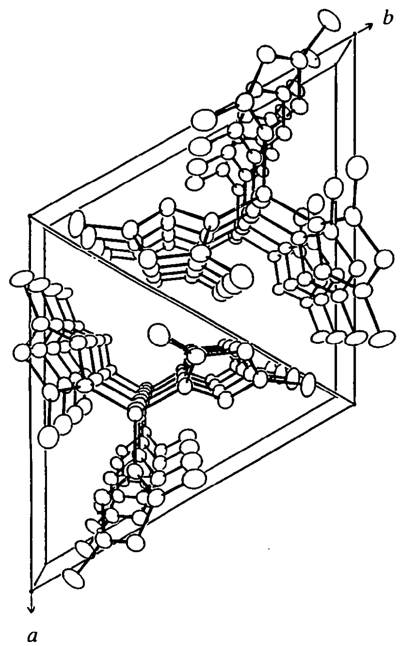
distorted tetrahedral geometry about Si, as indicated by the C—Si—N and N—Si—N′ angles.

In the crystal, individual molecules stack like badminton shuttlecocks along *c* (Fig. 2*a*), with the two distinct stacks shifted from each other by *c*/2. Fig. 2(*b*), a projection of a given layer along *c*, displays the $6_3$ symmetry.

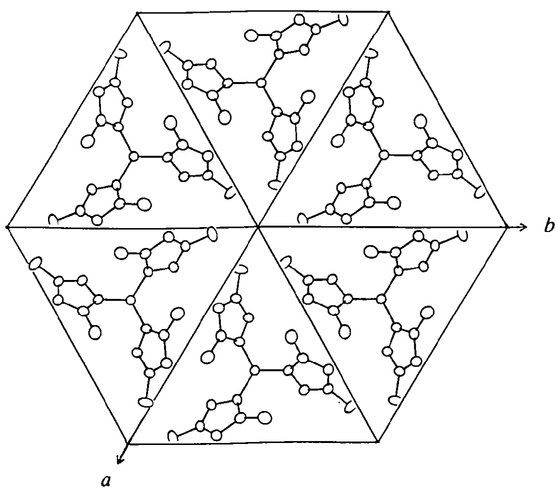
The dimethylpyrazolyl groups are bound asymmetrically to Si in a manner analogous to the bonding of pyrazole to P in (5) (Cobbledick & Einstein, 1975). The methyl group C(5) is situated so as to avoid close intramolecular contact with C(6), while the Si—N(1)—C(1) angle [137.6 (5)°] is much larger than the Si—N(1)—N(2) angle [111.8 (4)°]. In $P(Pz)_3$, (5), where Pz is 1-pyrazolyl, the corresponding P—N—C and P—N—N angles are 135.4 (4) and 115.0 (3)°, respectively. This large difference was attributed to interactions between the N(2) lone pair and vacant *d* orbitals on P, and to steric repulsion from the P···H—C(1) contact. A similar interpretation is possible for the present structure.

The pyrazole rings, planar to within ±0.004 Å, are canted with respect to the threefold axis to give the molecule a propeller-like shape. The C(6)—Si—N(1)—N(2) torsion angle [−46.2 (4)°] provides a measure of this twist. The pyrazole rings are also bent slightly from the C(6)—Si—N(1) plane as indicated by the deviation of the Si atom from the pyrazole plane (0.116 Å).

For the 3,5-dimethylpyrazole in (1), all the pyrazole bond lengths are within 3$\sigma$ and all the bond angles are within 2$\sigma$ of those in a metal complex containing a tris(3,5-dimethylpyrazol-1-yl)borate (Thompson, Marks & Ibers, 1979). The Si—N bond length of 1.745 (5) Å in (1) is slightly longer than




(a)




(b)

Fig. 2. (a) View of (1) showing the stacking along the c axis. (b) Projection of (1) along the c axis showing the packing in the ab plane.

those found in similar compounds. Two neutral compounds with distorted tetrahedral $SiN_4$ geometries have been reported. For tetrakis(methylamino)silane, the Si—N bond length is 1.701 (1) Å (Andersch & Jansen, 1990), while in di-2,2′-bipyridylsilicon, the Si—N bond lengths vary from 1.710 (8) to 1.73 (1) Å (Morancho, Pouvreau, Constant, Jaud & Galy, 1979). The Si—N distance in (1) compares favorably with the average length of a single bond between a three-coordinate N atom and a four-coordinate Si atom [1.748 (22) Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987].

## Experimental

Compound (1) was prepared by a trans-silylation technique, the reaction being carried out under nitrogen with the exclusion of water. 1.973 g (13 mmol) of trichloromethylsilane was added to 6.550 g (39 mmol) of trimethyl(3,5-dimethylpyrazol-1-yl)silane and stirred for 6 h. The mixture was then kept at 343 K for 3 d. The product was obtained by vacuum distillation. Colorless crystals of (1) were obtained by layering a solution of (1) in toluene with pentane.

*Crystal data*

| | |
|---|---|
| $C_{16}H_{24}N_6Si$ | Mo $K\alpha$ radiation |
| $M_r = 328.50$ | $\lambda = 0.71073$ Å |
| Hexagonal | Cell parameters from 25 reflections |
| $P6_3$ | $\theta = 10.32–18.23°$ |
| $a = 12.144$ (1) Å | $\mu = 0.12$ mm$^{-1}$ |
| $c = 7.814$ (1) Å | $T = 298$ K |
| $V = 998.0$ (2) Å$^3$ | Cleaved hexagonal plate |
| $Z = 2$ | 0.35 × 0.20 × 0.15 mm |
| $D_x = 1.093$ Mg m$^{-3}$ | Colorless |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.023$ |
| $\theta–2\theta$ scans | $\theta_{max} = 20°$ |
| Absorption correction: empirical | $h = 0 \rightarrow 11$ |
| $T_{min} = 0.987$, $T_{max} = 0.998$ | $k = 0 \rightarrow 11$ |
| 1093 measured reflections | $l = 0 \rightarrow 7$ |
| 496 independent reflections | 3 standard reflections monitored every 300 reflections |
| 376 observed reflections [$I > 3\sigma(I)$] | intensity decay: 2.3% |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$ |
| $R = 0.051$ | $(\Delta/\sigma)_{max} < 0.01$ |
| $wR = 0.049$ | $\Delta\rho_{max} = 0.175$ e Å$^{-3}$ |
| $S = 1.30$ | $\Delta\rho_{min} = -0.187$ e Å$^{-3}$ |
| 376 reflections | Extinction correction: none |
| 69 parameters | Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) |
| H-atom parameters not refined | |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Si | 2/3 | 1/3 | 1 | 3.32 (4) |
| N(1) | 0.6685 (3) | 0.2005 (4) | 0.9187 (7) | 3.5 (1) |
| N(2) | 0.7589 (3) | 0.1797 (3) | 1.0019 (8) | 4.2 (1) |
| C(1) | 0.6119 (5) | 0.1148 (5) | 0.788 (1) | 4.2 (2) |
| C(2) | 0.6654 (5) | 0.0386 (5) | 0.7847 (9) | 4.4 (2) |
| C(3) | 0.7535 (5) | 0.0820 (5) | 0.9185 (9) | 4.8 (2) |
| C(4) | 0.8349 (5) | 0.0288 (6) | 0.977 (2) | 7.2 (2) |
| C(5) | 0.5116 (7) | 0.1129 (5) | 0.674 (1) | 6.0 (2) |
| C(6) | 2/3 | 1/3 | 1.235 (2) | 4.6 (2) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Si—N(1) | 1.745 (5) | C(1)—C(2) | 1.37 (1) |
| Si—C(6) | 1.84 (1) | C(1)—C(5) | 1.50 (1) |
| N(1)—N(2) | 1.402 (7) | C(2)—C(3) | 1.40 (1) |
| N(1)—C(1) | 1.373 (9) | C(3)—C(4) | 1.50 (1) |
| N(2)—C(3) | 1.328 (8) | | |
| N(1)—Si—C(6) | 111.3 (2) | N(1)—C(1)—C(5) | 123.4 (7) |
| N(1)—Si—N(1′) | 107.5 (2) | C(2)—C(1)—C(5) | 129.3 (8) |
| Si—N(1)—N(2) | 111.8 (4) | C(1)—C(2)—C(3) | 105.3 (7) |
| Si—N(1)—C(1) | 137.6 (5) | N(2)—C(3)—C(2) | 112.9 (6) |
| N(2)—N(1)—C(1) | 110.5 (6) | N(2)—C(3)—C(4) | 119.2 (8) |
| N(1)—N(2)—C(3) | 104.0 (5) | C(2)—C(3)—C(4) | 127.8 (9) |
| N(1)—C(1)—C(2) | 107.3 (7) | | |
| C(6)—Si—N(1)—N(2) | −46.2 (4) | C(6)—Si—N(1)—C(1) | 139.2 (6) |

The refinement was by full-matrix least squares on *F*. Some H atoms were located from difference Fourier maps; others were placed at calculated positions (C—H 0.95 Å). H-atom displacement parameters were set at $B = 1.3(B_{eq}$ of the parent atom). H-atom parameters were not refined.

The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier techniques. Molecular graphics were obtained using *ORTEP*II (Johnson, 1976).

We thank the National Science Foundation for support (grant CHE-8919120) and the National Institutes of Health for an Instrumentation Grant (1510 RRO 1486 014).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# An Oxazolidinone Derivative of D-Furanose

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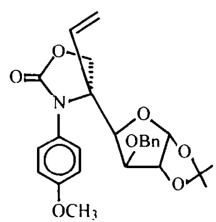
## Abstract

In the title compound, 4-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-3-(4-methoxyphenyl)-4-vinyloxazolidin-2-one, $C_{26}H_{29}NO_7$, the benzyloxy side chain extends axially with a *gauche–trans–gauche* conformation. The furanoid ring adopts a C(4)-*endo* envelope conformation. The isopropylidene ring has a half-chair conformation and the oxazolidinone ring has a minor O(5)-*exo* envelope conformation. Possible C—H···O interactions are observed.

## Comment

The crystal structure analysis of the title compound (I) was undertaken as part of our research programme on the synthesis of a novel immunosuppressant ISP-1 (Rama Rao, Gurjar, Rama Devi & Ravikumar, 1993). Bond lengths and angles (Table 2) are generallly close to normal (Allen *et al.*, 1987), except those involving the disordered C(7) atom. The benzyloxy side chain extends axially with a *gauche–trans–gauche* conformation [C(2)—C(3)—O(3)—C(20) 84.7 (5), C(3)—O(3)—C(20)—C(21) −179.4 (4), O(3)—C(20)—C(21)—C(22) 100.4 (6)°]. This side chain takes an *anti* orientation with respect to the isopropylidene ring [O(2)—C(2)—C(3)—O(3) −157.0 (4)°].




(I)

The furanoid ring adopts a C(4)-*endo* envelope conformation with asymmetry parameter $\Delta C_s$[C(4)] = 4.63° (Duax & Norton, 1975). The C(4) atom