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Azidotriphenylsilane: a new determination

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The title compound, (I), $C_{18}H_{15}N_3Si$, is monomeric with quasi-tetrahedral geometry around Si. The azide group ($-N_\alpha-N_\beta-N_\gamma$) is disordered. One form has ($N_\alpha-N_\beta$) > $d(N_\beta-N_\gamma)$; the other has $d(N_\alpha-N_\beta) < d(N_\beta-N_\gamma)$. In contrast, the mesityl analogue, (II), has $d(N_\alpha-N_\beta)$ only slightly less than $d(N_\beta-N_\gamma)$. As expected, on going from (I) to (II), $d(Si-N_\alpha)$, $d(Si-C)_{ave}$ and angle $(C-Si-C)_{ave}$ increase, while angle $(C-Si-N_\alpha)_{ave}$ decreases.

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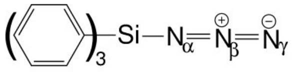
Key indicators

Single-crystal X-ray study
T = 220 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.121
Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Andose & Mislow (1974) have shown that replacing phenyl groups in Ph_3CH by mesityl (Mes = 2,4,6-trimethylphenyl) should result in small but significant changes caused by the strain due to the proximal CH_3 groups, *viz*. elongation of the central C—C bond and enlargement of the central C—C—C angle. In addition, for a given $Ph_3MX/(Mes)_3MX$ monomer pair (M = group 14 element; X = halide or pseudohalide) the interaction of distal CH_3 groups with X may well result in a longer $M-X$ bond. These changes are indeed found when comparing Ph_3SnI with $(Mes)_3SnI$ (Simard & Wharf, 1994), or Ph_3GeNCO (Tarkhova *et al.*, 1976) with $(Mes)_3GeNCO$ (Hihara *et al.*, 2000). A similar comparison was also attempted between the structures of Ph_3SiN_3, (I) (Corey *et al.*, 1973), and $(Mes)_3SiN_3$, (II) (Zigler *et al.*, 1989). Unfortunately, the 1973 structure of (I) was based on a very limited data set with a high R value (11%). In addition the final model was isotropic. Thus, to enable a more reliable comparison to be made, we now present a new determination of the structure of (I).



(I)

As reported earlier, (I) is monomeric (Fig. 1), with average C—Si—C angles [112.2 (6)°] greater than average C—Si—N angles [106.5 (7)°] (Table 1), average d(Si—C) = 1.859 (2) Å and d(Si—N1) = 1.7632 (15) Å, similar to results found earlier for Ph_3SiNCS (Sheldrick & Taylor, 1975). For (II) the corresponding data are 114.0 (1)°, 104.4 (1)°, 1.889 (3) Å, and 1.814 (2) Å, respectively. These changes on going from (I) to (II), in particular the 0.05 Å increase in d(Si—N1), are clearly consistent with those reported above for other Ph/Mes analog pairs.

In (I), N_β and N_γ of the azide group are disordered (50/50), component (1) having d(N1—N21) > d(N21—N3)] with Si—N1—N21 = 123.2 (8)° and N1—N21—N31 = 170.70 (17)° while component (2) has d(N1—N22) < d(N22—N32), Si—N1—N22 = 124.70 (10)° and N1—N22—N32 = 173 (2)°.

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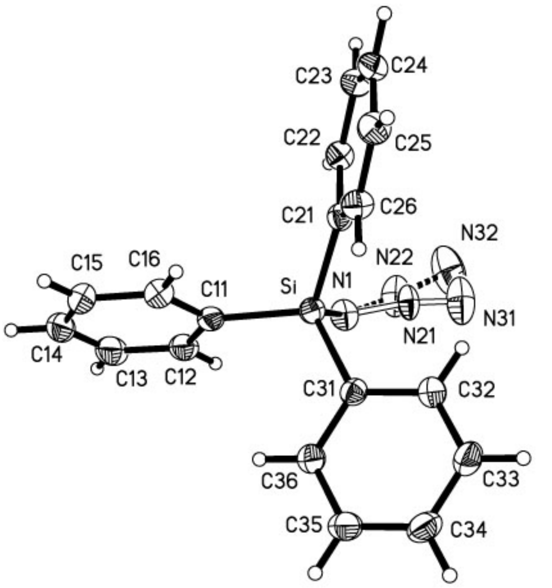


Figure 1
ORTEP (Johnson, 1976) view of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

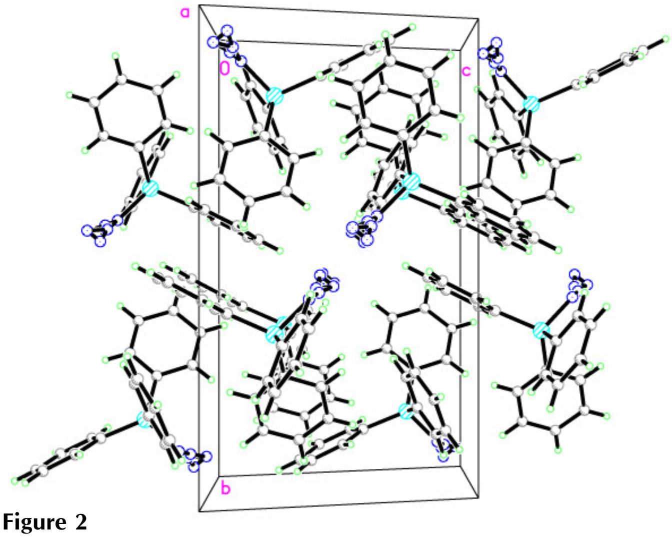
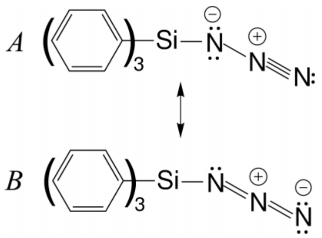


Figure 2
Packing diagram, viewed down the *a* axis. Note the space available for adjacent terminal N atoms in the centre of the cell.

The bonding in covalent silyl azides is usually discussed in terms of two resonance forms, *A* and *B*, with their relative contributions assessed by changes in N—N bond distances. Thus (1) would appear to have a greater contribution from form *A* while the reverse is the case for (2). It is thus possible that molecule (I) has at least two or more quasi-degenerate ground states with slightly different configurations. Often, one configuration will be selected in the solid state to fit the exigences of crystal packing. In this case (Fig. 2), while the Ph_3Si—N1 moiety has a fixed geometry, the azide unit is more plastic and deformable. Indeed, interatomic distances between neighboring terminal N atoms; N31$\cdots$N31^{i}, 4.50 (3); N31$\cdots$N32^{i}, 4.51 (2); N32$\cdots$N32^{i}, 4.60 (3) Å [symmetry code: (i) $2 - x$, $-y$, $-z$]; are all greater than van der Waals, indicating no preference for (1) or (2), or perhaps even other intermediate configurations. This may also account for the large $U_{\rm eq}$ values noted for atoms N31 and N32.



Experimental

The title compound was prepared by a literature method (Schulz *et al.*, 1996). Suitable crystals were obtained by recrystallization from a hexane solution.

Crystal data

$C_{18}H_{15}N_3Si$
$M_r = 301.42$
Monoclinic, $P2_1/n$
$a = 9.6708$ (2) Å
$b = 17.0961$ (3) Å
$c = 10.3028$ (2) Å
$\beta = 109.665$ (1)°
$V = 1604.04$ (5) Å^3
$Z = 4$

$D_x = 1.248$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 14448 reflections
$\theta = 2.6$–72.6°
$\mu = 1.28$ mm^{-1}
$T = 220$ (2) K
Block, colorless
0.40 × 0.26 × 0.13 mm

Data collection

Bruker SMART 2K/Platform diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.705$, $T_{\rm max} = 0.847$
19377 measured reflections

3164 independent reflections
2756 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 72.8°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.121$
$S = 1.04$
3164 reflections
217 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 0.1083P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Si—N1	1.7632 (15)	N1—N22	1.09 (2)
Si—C31	1.8546 (15)	N1—N21	1.284 (17)
Si—C11	1.8588 (15)	N21—N31	1.06 (2)
Si—C21	1.8636 (14)	N22—N32	1.24 (3)
N1—Si—C31	107.94 (7)	C11—Si—C21	112.04 (6)
N1—Si—C11	103.17 (7)	N22—N1—Si	124.70 (11)
C31—Si—C11	112.60 (6)	N21—N1—Si	123.2 (8)
N1—Si—C21	108.34 (7)	N31—N21—N1	170.70 (17)
C31—Si—C21	112.18 (6)	N1—N22—N32	173 (2)
C31—Si—N1—N22	−80.60 (13)	N1—Si—C11—C12	20.35 (14)
C11—Si—N1—N22	160.00 (13)	N1—Si—C11—C16	−158.94 (13)
C21—Si—N1—N22	41.10 (13)	N1—Si—C21—C22	36.53 (13)
C31—Si—N1—N21	−69.8 (9)	N1—Si—C21—C26	−147.91 (12)
C11—Si—N1—N21	170.8 (9)	N1—Si—C31—C36	−101.42 (13)
C21—Si—N1—N21	51.9 (9)	N1—Si—C31—C32	75.08 (14)

The H atoms were positioned geometrically (C—H 0.94 Å) and were included in the refinement in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). The azide group could not be described without using a disorder model. Two sets of atoms were defined. The occupancy factor was initially refined and was then fixed at 0.50 for each set in the final cycles.

Data collection: *SMART* (Bruker, 1999); cell refinement and data reduction: *SAINT* (Bruker, 1999); structure solution : *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (local program).

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