4-Phenylthio-2-(triisopropylsilyl)but-2-enenitrile

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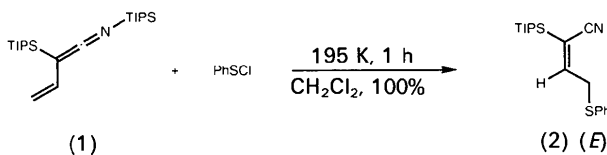*1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium*

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Abstract. $C_{19}H_{29}NSSi$, $M_r = 331 \cdot 60$, monoclinic, $P2_1/n$, $a = 10 \cdot 428$ (3), $b = 24 \cdot 094$ (7), $c = 16 \cdot 197$ (4) Å, $\beta = 98 \cdot 50$ (2)°, $V = 4025$ (2) Å^3, $Z = 8$, $D_x = 1 \cdot 09$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 2 \cdot 15$ cm^{-1}, $F(000) = 1440$, $T = 291$ K, $R = 0 \cdot 053$ for 3206 observed reflections. The E configuration about the double bond is established. The two independent molecules have a similar geometry. In each, the ethylenic system is essentially planar with deviations less than $0 \cdot 020$ Å from the best mean plane through C1, C2, C3, C4 and Si. To relieve the steric strain, the $C(sp^2)$—Si bond [mean value $1 \cdot 898$ (5) Å] is stretched and some angles about the double bond deviate significantly from the ideal trigonal value.

Experimental. The *N*-silylated vinylketenimine (1) reacts regiospecifically with phenylsulfenyl chloride at the γ position to give in quantitative yield the $\alpha\beta$-unsaturated nitrile (2) (Roekens, 1990). The ^{13}C NMR spectrum shows a coupling between the nitrile carbon and the olefinic proton. The coupling constant of 17 Hz is consistent with the E configuration about the double bond, that is the triisopropylsilyl group (TIPS) *trans* to the alkyl substituent. The X-ray analysis was undertaken in order to establish unambiguously this stereochemistry.

Crystals were obtained by evaporation from ethanol. D_m not measured. Parallelepiped crystal with dimensions $0 \cdot 20 \times 0 \cdot 40 \times 0 \cdot 40$ mm. Lattice parameters refined using 24 reflections in the range $10 \leq 2\theta \leq 25°$. Huber four-circle diffractometer, monochromatized Mo $K\alpha$ radiation. 5956 independent reflections with $\sin\theta/\lambda \leq 0 \cdot 56$ Å^{-1}; $0 \leq h \leq 11$,

$0 \leq k \leq 24$, $-18 \leq l \leq 18$, 3206 with $I \geq 2 \cdot 5\sigma(I)$. Standard reflection $3\overline{5}5$ checked every 50 reflections, no significant deviation. Structure solved by *SHELXS*86 (Sheldrick, 1985). H atom on C(2) from difference Fourier synthesis; all others in idealized positions (C—H = $1 \cdot 08$ Å, H—C—H = $109 \cdot 5°$). Anisotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) using F; H atoms isotropic with common refined temperature factor. $w = 1/(\sigma^2 + 0 \cdot 00264F^2)$. $R = 0 \cdot 053$, $wR = 0 \cdot 059$ for 3206 observed reflections. Final max. shift/e.s.d. $= 0 \cdot 31$ (U_{13} of C21B). $S = 1 \cdot 09$. Max. and min. heights in final difference Fourier synthesis $= 0 \cdot 22$ and $-0 \cdot 22$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The atomic parameters are given in Table 1.* The bond lengths and angles are listed in Table 2. Fig. 1 is a stereoscopic view of the molecule, showing the numbering of the atoms (*PLUTO*; Motherwell & Clegg, 1978).

Related literature. The Si—$C(sp^2)$ bond lengths reported for $H_3SiCH{=}CH_2$ and $PhSiH_3$ are $1 \cdot 853$ Å (microwave spectra) (O'Reilly & Pierce, 1961) and $1 \cdot 843$ Å (electron diffraction) (Keidel & Bauer, 1956), respectively. Si—C$=$C systems more similar to that discussed here are 2-cyano-1-(triphenyl-silyl)hex-1-ene (Fallon, Fitzmaurice, Jackson & Perlmutter, 1986) and 3-(dimethoxysilyl)-2,4-di-phenyl-1,1,4-tris(trimethylsilyl)but-2-ene (Ishikawa, Sugisawa, Akimoto, Matsusaki, Kamitori, Hirotsu & Higuchi, 1986). In these two molecules, the Si—$C(sp^2)$ bond lengths are $1 \cdot 869$ (3) and $1 \cdot 854$ (4) Å, respectively (Allen, Kennard & Taylor, 1983). In

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperaure factors* ($\mathring{A}^2$)

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

	x	y	z	B_{eq}
Molecule A				
C1	2084 (5)	7334 (2)	3548 (3)	5·60 (11)
C2	2001 (4)	7115 (2)	4359 (3)	4·22 (9)
C3	2776 (5)	6698 (2)	4647 (3)	4·79 (10)
C4	3773 (5)	6426 (2)	4195 (3)	5·94 (11)
Si	733 (1)	7424 (1)	4953 (1)	3·94 (2)
C6	−828 (4)	7039 (2)	4619 (3)	5·07 (10)
C7	−1336 (5)	7107 (3)	3688 (3)	7·48 (14)
C8	−702 (5)	6420 (2)	4834 (4)	7·44 (14)
C9	550 (5)	8173 (2)	4629 (3)	5·22 (11)
C10	−608 (5)	8448 (2)	4921 (3)	6·94 (13)
C11	1763 (6)	8522 (2)	4850 (5)	8·81 (17)
C12	1305 (5)	7301 (2)	6090 (3)	4·57 (10)
C13	263 (6)	7428 (2)	6644 (3)	7·05 (13)
C14	2579 (6)	7585 (3)	6441 (3)	7·61 (14)
N15	2099 (5)	7532 (2)	2912 (3)	8·86 (14)
S16	5379 (1)	6468 (1)	4821 (1)	6·29 (3)
C17	5604 (4)	7197 (2)	4935 (3)	4·95 (10)
C18	5343 (5)	7559 (3)	4264 (4)	6·32 (13)
C19	5584 (6)	8123 (3)	4403 (5)	7·86 (18)
C20	6090 (7)	8318 (3)	5175 (6)	8·36 (18)
C21	6342 (6)	7949 (3)	5822 (4)	7·47 (16)
C22	6101 (5)	7393 (3)	5718 (3)	5·88 (12)
Molecule B				
C1	−1915 (5)	5074 (2)	1150 (3)	5·63 (12)
C2	−2054 (4)	5281 (2)	1956 (3)	3·94 (9)
C3	−1314 (4)	5711 (2)	2260 (3)	4·73 (10)
C4	−301 (4)	5999 (2)	1850 (3)	5·89 (11)
Si	−3323 (1)	4947 (1)	2524 (1)	3·69 (2)
C6	−4927 (4)	5274 (2)	2109 (3)	4·77 (10)
C7	−5343 (5)	5163 (2)	1176 (3)	6·79 (13)
C8	−4907 (5)	5902 (2)	2277 (3)	6·35 (13)
C9	−2869 (4)	5117 (2)	3663 (3)	4·32 (9)
C10	−3959 (5)	4968 (2)	4176 (3)	5·97 (12)
C11	−1594 (5)	4871 (3)	4078 (3)	6·96 (13)
C12	−3339 (5)	4190 (2)	2243 (3)	5·21 (10)
C13	−4337 (6)	3851 (2)	2657 (4)	7·37 (14)
C14	−2021 (6)	3908 (2)	2372 (4)	7·86 (15)
N15	−1832 (5)	4885 (2)	505 (3)	8·27 (13)
S16	1277 (1)	5909 (1)	2491 (1)	6·38 (3)
C17	1493 (4)	5182 (2)	2480 (3)	5·09 (11)
C18	1816 (5)	4908 (3)	3231 (4)	6·97 (15)
C19	2059 (7)	4336 (4)	3222 (6)	10·46 (23)
C20	1934 (8)	4064 (4)	2458 (9)	11·69 (29)
C21	1625 (7)	4353 (5)	1756 (6)	10·03 (25)
C22	1403 (5)	4897 (3)	1756 (4)	6·67 (14)

Table 2. *Bond distances* ($\mathring{A}$) *and angles* (°)

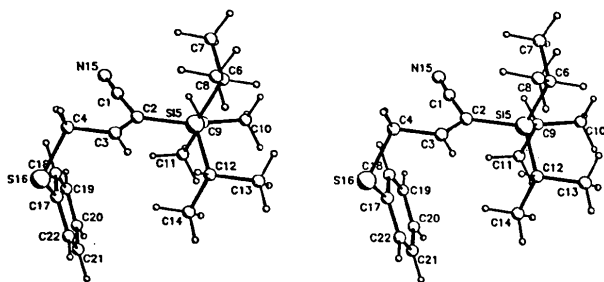|	A	B
C3—C2	1·329 (7)	1·341 (6)
C1—C2	1·430 (7)	1·426 (7)
Si—C2	1·899 (5)	1·898 (5)
C4—C3	1·507 (7)	1·498 (7)
N15—C1	1·138 (7)	1·155 (7)
C6—Si	1·883 (5)	1·880 (4)
C9—Si	1·882 (5)	1·881 (4)
C12—Si	1·874 (4)	1·881 (5)
C7—C6	1·532 (7)	1·533 (7)
C8—C6	1·531 (8)	1·537 (7)
C10—C9	1·512 (8)	1·546 (7)
C11—C9	1·517 (8)	1·518 (7)
C13—C12	1·538 (8)	1·551 (8)
C14—C12	1·528 (7)	1·519 (8)
S16—C4	1·828 (5)	1·824 (5)
C17—S16	1·778 (5)	1·768 (5)
C18—C17	1·388 (8)	1·381 (8)
C22—C17	1·381 (7)	1·350 (8)
C19—C18	1·396 (10)	1·402 (12)
C20—C19	1·366 (12)	1·390 (17)
C21—C20	1·369 (11)	1·331 (16)
C22—C21	1·369 (10)	1·332 (13)
C1—C2—C3	119·0 (5)	118·4 (4)
Si—C2—C3	123·5 (4)	123·7 (4)
Si—C2—C1	117·5 (3)	117·9 (3)
C4—C3—C2	125·9 (5)	126·9 (5)
N15—C1—C2	175·9 (6)	176·9 (6)
C6—Si—C2	107·3 (2)	107·3 (2)
C9—Si—C2	106·5 (2)	106·9 (2)
C9—Si—C6	110·2 (2)	110·0 (2)
C12—Si—C2	107·0 (2)	106·0 (2)
C12—Si—C6	109·9 (2)	110·1 (2)
C12—Si—C9	115·5 (2)	116·1 (2)
C7—C6—Si	112·8 (4)	112·7 (3)
C8—C6—Si	111·9 (3)	111·1 (3)
C8—C6—C7	109·6 (4)	109·9 (4)
C10—C9—Si	112·7 (4)	112·2 (3)
C11—C9—Si	114·8 (3)	115·3 (3)
C11—C9—C10	111·1 (4)	109·8 (4)
C13—C12—Si	113·1 (3)	112·9 (4)
C14—C12—Si	115·3 (3)	115·1 (3)
C14—C12—C13	110·1 (4)	110·9 (4)
S16—C4—C3	110·3 (3)	109·2 (3)
C17—S16—C4	102·0 (2)	102·6 (2)
C18—C17—S16	122·2 (4)	118·7 (4)
C22—C17—S16	117·3 (4)	121·3 (5)
C22—C17—C18	120·5 (5)	120·0 (6)
C19—C18—C17	118·5 (5)	118·8 (6)
C20—C19—C18	121·1 (7)	118·7 (8)
C21—C20—C19	118·8 (7)	119·5 (9)
C22—C21—C20	122·0 (6)	122·4 (9)
C21—C22—C17	119·0 (5)	120·7 (7)

Fig. 1. Stereoscopic view of the molecule.

very overcrowded systems, for example tetrakis(tri-methylsilyl)ethylene (Sakurai, Nakadaira, Tobita, Ito, Toriumi & Ito, 1982), an Si—C(sp^2) bond length as long as 1·918 (2) Å has been observed.

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