Monoclinic
$P2_1/c$
$a = 11.549$ (3) Å
$b = 3.756$ (1) Å
$c = 16.442$ (8) Å
$\beta = 104.94$ (3)°
$V = 689.1$ (4) Å^3
$Z = 4$
$D_x = 1.572$ Mg m^{-3}
$D_m = 1.58$ Mg m^{-3}

Cell parameters from 25
 reflections
$\theta = 5.42$–$9.50°$
$\mu = 0.1151$ mm^{-1}
$T = 298$ K
Prism
$0.5 \times 0.4 \times 0.25$ mm
Colourless
Crystal source: from water
 solution

Data collection

Enraf–Nonius CAD-4
 diffractometer
$\omega/2\theta$ scans
Absorption correction:
 empirical
$T_{min} = 0.8358$, $T_{max} =$
 0.9992
1309 measured reflections
1262 independent reflections

536 observed reflections
 $[F_o > 3\sigma(F_o)]$
$R_{int} = 0.032$
$\theta_{max} = 24°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 18$
3 standard reflections
 frequency: 150 min
 intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.045$
$S = 0.685$
535 reflections
125 parameters
Only coordinates of H atoms
 refined

If $F < 61$ then $w = 1$, if
 $F \geq 61$ then $w = (61/F)^2$,
 if $F^2 < 3\sigma(F^2)$ then $w = 0$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.169$ e Å^{-3}
$\Delta\rho_{min} = -0.189$ e Å^{-3}
Atomic scattering factors
 from *International Tables
 for X-ray Crystallography*
 (1974, Vol. IV)

O(2)—C(2)—N(1)	124.9 (4)	C(12)—C(13)—C(14)	117.5 (5)
O(2)—C(2)—C(12)	130.2 (5)	C(13)—C(14)—C(15)	122.0 (6)
N(1)—C(2)—C(12)	104.8 (4)	C(14)—C(15)—C(16)	120.2 (5)
C(11)—C(16)—C(15)	118.3 (5)		

Program used throughout the analysis: *MolEN* (Fair, 1990). Program used to solve the structure: *MULTAN*11/82 (Main *et al.*, 1982).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry and torsion angles, have been deposited with the IUCr (Reference: AS1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(10)	0.8854 (3)	0.195 (1)	0.2014 (2)	3.83 (8)
O(1)	0.9829 (3)	0.102 (1)	0.3745 (1)	3.49 (8)
O(2)	0.6619 (3)	0.557 (1)	0.1790 (2)	4.66 (9)
N(1)	0.8393 (3)	0.336 (1)	0.2635 (3)	3.02 (9)
C(1)	0.8895 (4)	0.262 (1)	0.3477 (3)	2.7 (1)
C(2)	0.7250 (4)	0.486 (1)	0.2480 (3)	2.8 (1)
C(11)	0.8037 (4)	0.403 (1)	0.3915 (3)	2.5 (1)
C(12)	0.7038 (4)	0.535 (1)	0.3317 (3)	2.7 (1)
C(13)	0.6074 (4)	0.673 (2)	0.3556 (3)	3.5 (1)
C(14)	0.6132 (4)	0.677 (2)	0.4403 (3)	4.1 (1)
C(15)	0.7122 (5)	0.549 (2)	0.5002 (3)	4.0 (1)
C(16)	0.8084 (4)	0.409 (1)	0.4758 (3)	3.4 (1)

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

O(10)—N(1)	1.374 (5)	C(11)—C(12)	1.399 (6)
O(1)—C(1)	1.213 (5)	C(11)—C(16)	1.372 (7)
O(2)—C(2)	1.209 (5)	C(12)—C(13)	1.374 (7)
N(1)—C(1)	1.384 (6)	C(13)—C(14)	1.377 (8)
N(1)—C(2)	1.397 (8)	C(14)—C(15)	1.388 (8)
C(1)—C(11)	1.467 (6)	C(15)—C(16)	1.379 (8)
C(2)—C(12)	1.470 (7)		
O(10)—N(1)—C(1)	121.5 (4)	C(1)—C(11)—C(12)	108.8 (4)
O(10)—N(1)—C(2)	123.3 (4)	C(1)—C(11)—C(16)	130.2 (5)
C(1)—N(1)—C(2)	113.4 (4)	C(12)—C(11)—C(16)	121.0 (5)
O(1)—C(1)—N(1)	124.6 (5)	C(2)—C(12)—C(11)	108.0 (4)
O(1)—C(1)—C(11)	130.6 (4)	C(2)—C(12)—C(13)	131.0 (5)
N(1)—C(1)—C(11)	104.8 (4)	C(11)—C(12)—C(13)	121.0 (5)

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A Branched Polysilane

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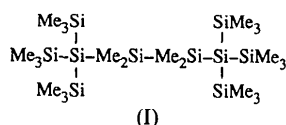
Abstract

2,2,5,5-Tetrakis(trimethylsilyl)-1,1,1,3,3,4,4,6,6,6-deca-methylhexasilane, $C_{22}H_{66}Si_{10}$, is a polysilane in which the longest chain is made up of six Si atoms and branching occurs at the second and fifth Si atoms. Each of the two central Si atoms is bonded to a tris(trimethylsilyl)silyl group in an *anti* arrangement. Bond lengths and angles are sufficiently close to normal to indicate that the molecule is relatively unstrained.

Comment

Molecules built up from chains of Si—Si bonds, called polysilanes, have come under increased scrutiny because of their unusual electronic properties (West, 1989). The low-lying σ–σ^* excitations convey properties normally associated with conjugated π systems, such as electrical conduction and nonlinear optics. Electron delocalization is dependent on the number of Si—Si bonds and on their relative orientations (*anti* or *gauche*). Consequently, structural information is useful in understanding their electronic properties. Structures have been reported for several linear chains and for cyclic and polycyclic systems (Sheldrick, 1989). Very little information has been obtained for branched systems, in which there are multiple polysilyl routes and steric crowding may become important. We have prepared ($Me_3Si)_3Si$—Me_2Si—Me_2Si—$Si(Me_3Si)_3$, (I), and carried out the determination of its crystal structure. This molecule may be named either 1,2-bis[tris(trimethylsilyl)silyl]tetramethyldisilane to emphasize the substituted disilane core or 2,2,5,5-tetrakis(trimethylsilyl)-1,1,1,3,3,4,4,6,6,6-decamethylhexasilane to emphasize the longest chain. The molecule is the permethyl polysilyl analogue of di(*tert*-butyl)ethane.

$$
\begin{array}{ccc}
Me_3Si & & SiMe_3 \\
| & & | \\
Me_3Si\text{--}Si\text{--}Me_2Si\text{--}Me_2Si\text{--}Si\text{--}SiMe_3 \\
| & & | \\
Me_3Si & & SiMe_3
\end{array}
$$
(I)

The two tris(trimethylsilyl)silyl groups (the permethyl silicon analogue of the *tert*-butyl group) are arranged in an *anti* fashion on the central disilane. The Si1—Si4—Si4'—Si1' dihedral angle is 180.0°. There is little strain across the central Si—Si bond, as its bond length (Si4—Si4') of 2.374 Å is not appreciably different from the average length of the other four Si—Si bonds (2.359 Å). These values are marginally larger than that of 2.340 Å found in hexamethyldisilane (Beagley, Monaghan &
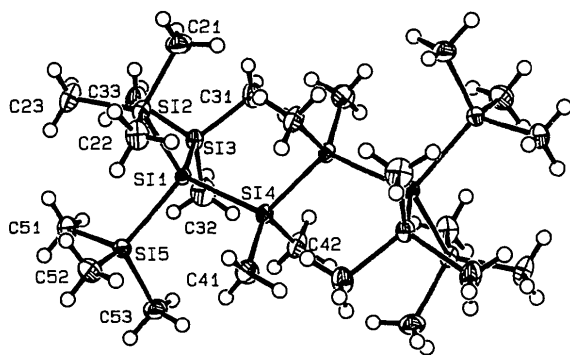

Fig. 1. Molecular structure and numbering scheme for 2,2,5,5-tetrakis-(trimethylsilyl)-1,1,1,3,3,4,4,6,6,6-decamethylhexasilane (50% probability level for ellipsoids).

Hewitt, 1971), are similar to the gas-phase value of 2.361 Å found in tetrakis(trimethylsilyl)silane (Bartell, Clippard & Boates, 1970), and are clearly smaller than the value of 2.697 Å found in tetra-*tert*-butyldisilane (Wiberg, Schuster, Simon & Peters, 1986). The average of the 11 Si—C bond lengths is normal at 1.877 Å, and the 33 C—H bond lengths average 0.94 Å. The seven Si—Si—Si bond angles average 110.5°, the 13 Si—Si—C angles average 110.1°, and the 10 C—Si—C angles average 107.9°. Despite the presence of six quaternary centers in a row along the hexasilane backbone, the bond lengths and angles indicate that there is little strain present in the molecule. The normally long Si—Si and Si—C bond lengths adequately compensate for the high level of substitution at this level of branching.

Experimental

Crystal data

$C_{22}H_{66}Si_{10}$	Mo $K\alpha$ radiation
$M_r = 611.62$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 9.138\ (2)$ Å	$\theta = 19.2$–$23.7°$
$b = 9.172\ (3)$ Å	$\mu = 0.33\ mm^{-1}$
$c = 13.598\ (6)$ Å	$T = 153$ K
$\alpha = 103.34\ (3)°$	Translucent prismatic
$\beta = 92.01\ (3)°$	$0.47 \times 0.45 \times 0.20$ mm
$\gamma = 114.30\ (2)°$	Off-white
$V = 1000\ (1)$ Å^3	
$Z = 1$	
$D_x = 1.016$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.027$
	$\theta_{max} = 26.0°$
$\omega/2\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction:	$k = -11 \rightarrow 11$
analytical	$l = -16 \rightarrow 0$
$T_{min} = 0.86,\ T_{max} = 0.91$	3 standard reflections
4079 measured reflections	frequency: 90 min
3907 independent reflections	intensity decay: none
3388 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.38$ e Å^{-3}
$R = 0.024$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$wR = 0.033$	Extinction correction:
$S = 1.62$	secondary
3388 reflections	Extinction coefficient:
278 parameters	0.26726×10^{-5}
All H-atom parameters	Atomic scattering factors
refined	from *International Tables*
$w = 4F_o^2/\sigma^2(F_o^2)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.01$	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^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}
Si1	0.19566 (4)	0.65391 (4)	0.21768 (3)	1.31 (1)
Si2	0.42230 (4)	0.87138 (5)	0.18621 (3)	1.73 (1)
Si3	0.05154 (4)	0.76677 (5)	0.32646 (3)	1.75 (1)
Si4	0.02440 (4)	0.45092 (4)	0.06946 (3)	1.53 (1)
Si5	0.29317 (5)	0.51649 (5)	0.31088 (3)	1.85 (1)
C21	0.3591 (2)	1.0206 (2)	0.1447 (1)	2.81 (5)
C22	0.5281 (2)	0.7885 (2)	0.0883 (1)	2.81 (5)
C23	0.5747 (2)	0.9919 (2)	0.3049 (1)	2.92 (5)
C31	−0.0789 (2)	0.8337 (2)	0.2565 (1)	2.56 (5)
C32	−0.0830 (2)	0.6129 (2)	0.3917 (1)	3.05 (5)
C33	0.1959 (2)	0.9546 (2)	0.4278 (1)	2.85 (5)
C41	0.1150 (2)	0.3009 (2)	0.0238 (1)	2.73 (5)
C42	−0.1737 (2)	0.3359 (2)	0.1143 (1)	2.52 (5)
C51	0.3738 (2)	0.6445 (2)	0.4469 (1)	2.96 (5)
C52	0.4634 (2)	0.4799 (2)	0.2546 (2)	3.02 (6)
C53	0.1286 (2)	0.3119 (2)	0.3149 (1)	2.82 (5)

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

Si1—Si2	2.3467 (9)	Si3—C32	1.875 (2)
Si1—Si3	2.3550 (9)	Si3—C33	1.874 (2)
Si1—Si4	2.372 (1)	Si4—Si4	2.374 (1)
Si1—Si5	2.3604 (8)	Si4—C41	1.882 (2)
Si2—C21	1.874 (2)	Si4—C42	1.888 (2)
Si2—C22	1.874 (2)	Si5—C51	1.879 (2)
Si2—C23	1.876 (2)	Si5—C52	1.875 (2)
Si3—C31	1.869 (2)	Si5—C53	1.875 (2)
Si2—Si1—Si3	109.04 (4)	C31—Si3—C32	107.70 (9)
Si2—Si1—Si4	115.02 (4)	C31—Si3—C33	107.10 (9)
Si2—Si1—Si5	107.38 (3)	C32—Si3—C33	107.89 (9)
Si3—Si1—Si4	111.92 (3)	Si1—Si4—Si4	116.80 (4)
Si3—Si1—Si5	105.94 (3)	Si1—Si4—C41	108.06 (6)
Si4—Si1—Si5	107.03 (4)	Si1—Si4—C42	105.25 (6)
Si1—Si2—C21	110.09 (6)	Si4—Si4—C41	108.54 (6)
Si1—Si2—C22	110.77 (7)	Si4—Si4—C42	109.76 (6)
Si1—Si2—C23	111.07 (7)	C41—Si4—C42	108.11 (9)
C21—Si2—C22	111.01 (9)	Si1—Si5—C51	110.82 (6)
C21—Si2—C23	107.02 (9)	Si1—Si5—C52	111.17 (7)
C22—Si2—C23	106.76 (9)	Si1—Si5—C53	111.64 (6)
Si1—Si3—C31	112.35 (6)	C51—Si5—C52	107.24 (9)
Si1—Si3—C32	111.29 (7)	C51—Si5—C53	107.01 (9)
Si1—Si3—C33	110.32 (6)	C52—Si5—C53	108.76 (9)

The space group was determined from packing considerations and a statistical analysis of intensity distribution. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1989).

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(Z)-{4-[1-Cyano-3-(diethyliminio)-1-propenyl]phenyl}dicyanomethanide, a Novel 'Blue Window' Zwitterionic Molecule for Non-Linear Optics

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Abstract

The crystal structure of the title compound, $C_{17}H_{16}N_4$, (1), has been elucidated. The molecule is shown to be planar with a highly delocalized π system between the two zwitterionic charge centres. This rationalizes the strong solution dipole moment exhibited by this molecule (45 D) and its high measured first hyperpolarizability (190 × 10^{-30} e.s.u.). The electronic spectrum of the molecule consists of strong transitions in the visible region between 500 and 700 nm, but with an absence of absorption to either side. The unusually low optical absorption between 450 and 470 nm suggests that the description 'blue window material' may be applied in relation to frequency doubling applications

Comment

There are now numerous organic non-linear optical materials showing large second-order non-linearities (Prasad & Williams, 1991). The basic structural requirements for second-order molecules have been known