organic compounds

1,4-Bis[2,2-bis(trimethylsilyl)ethenyl]-benzene

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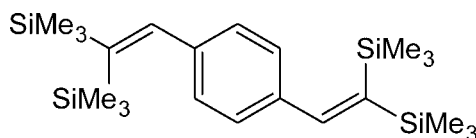
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The molecules of the title compound, $C_{22}H_{42}Si_4$, are centrosymmetric. van der Waals interactions determine the crystal structure.

Related literature

For related literature, see: Cuadrado *et al.* (2004); Hodgson *et al.* (1997); Inoue *et al.* (2001); Inoue *et al.* (2002); Pawluć *et al.* (2007); Uhl & Breher (2000).

Experimental

Crystal data

$C_{22}H_{42}Si_4$	V = 2691.2 (4) Å^3
M_r = 418.92	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 31.050 (2) Å	μ = 0.23 mm^{-1}
b = 6.5882 (7) Å	T = 100 (1) K
c = 13.1661 (14) Å	$0.5 \times 0.05 \times 0.05$ mm
β = 92.293 (7)°	

Data collection

Kuma KM-4-CCD four-circle diffractometer	13212 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	3547 independent reflections
	2579 reflections with $I > 2\sigma(I)$
T_{min} = 0.804, T_{max} = 0.989	R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.083	
S = 1.00	
3547 reflections	$\Delta\rho_{max}$ = 0.37 e Å^{-3}
190 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2244).

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supplementary materials

1,4-Bis[2,2-bis(trimethylsilyl)ethenyl]benzene

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Comment

1,1-Bis(silyl)-2-arylalkenes constitute an important class of organosilicon reagents which are currently widely used as potential intermediates in the organic and organometallic syntheses. Their use as precursors for the preparation of ketones (Inoue *et al.*, 2002), dibromostyrenes (Pawluć *et al.*, 2007) as well as a variety of important organosilicon intermediates such as acylsilanes (Inoue *et al.*, 2001), epoxysilanes (Hodgson *et al.*, 1997) silyl enol ethers (Cuadrado *et al.*, 2004) *etc*, greatly stimulates their synthetic advancements. Although considerable effort has been made to the characterization of 1,1-bis(silyl)-2-arylalkenes, determination of their crystal structures remains almost unexplored. Here we report the crystal structure of 1,4-bis(2,2-bis(trimethylsilyl)ethenyl)benzene (1). To the best of our knowledge, this is the first example of structurally characterized 1,1-bis(silyl)-2-arylalkene without additional substituent in 2-position. The closest structure known contains *t*-butyl-Al instead of one $SiMe_3$ group: 1,4-bis{2-di(*tert*-butyl)aluminium-2-trimethylsilyl-ethenyl}benzene (Uhl & Breher, 2000).

The overall conformation of the molecule **1** (Fig. 1) can be characterized by the dihedral angle between the benzene ring (planar within 0.0051 (7) Å) and approximately planar C11, C12, Si1, Si2 fragment (maximum deviation of 0.017 (1) Å); this angle is equal 51.75 (6)°.

The Si—C bonds differ in their lengths depending on the hybridization of the carbon atom; the mean values are 1.871 (4)Å for C(sp^3) and 1.892 (2)Å for C(sp^2). The silylethenyl substiuent changes the intraannular angles in benzene ring: the *ipso* angle is sharpened to 117.96 (11)°, while the neighbouring angle is widened to 121.19 (12)°.

Crystal packing (Fig. 2) is determined mainly by van der Waals interactions.

Experimental

A mixture consisting of 67.0 mg (0.30 mmol) of palladium(II) acetate, 157.2 mg (0.6 mmol) of triphenylphosphine, 1.70 g of silver nitrate (10 mmol), 5 mmol of 1,4-diiodobenzene, 10 mmol (1.72 g) of 1,1-bis(trimethylsilyl)ethene, 2.80 ml (20 mmol) of triethylamine and 30 ml of acetonitrile was placed in 50 ml, two-necked, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 80ºC for 2 h. After cooling to room temperature, the reaction mixture was added to water (50 ml) and extracted twice with 30 ml of pentane. The combined organic layers were dried ($MgSO_4$) and the crude product obtained was then purified by column chromatography (silica gel/pentane) to give pure product. (2.01 g, 96%, white crystals) ^{1}H NMR ($CDCl_3$,) δ(p.p.m.): −0.01 (s, 18H, $SiCH_3$), 0.18 (s, 18H, $SiCH_3$), 7.12 (s, 4H, Ar), 7.72 (s, 2H, =CH—). ^{13}C NMR ($CDCl_3$,) δ(p.p.m.): 0.5 ($SiCH_3$), 2.1 ($SiCH_3$), 127.4, 141.4 (Ar), 146.3 (—CH=), 154.7 (>C=). MS (EI) *m/z* (*rel*. int.): 418 (*M*+ 10%), 345 (15), 257 (10), 171 (100), 131 (10), 73 (15). HRMS calcd for $C_{22}H_{42}Si_4$: 418.2363, found: 418.2348.

supplementary materials

Refinement

Hydrogen atoms were found in the difference Fourier maps; the positional parameters of all hydrogen atoms were freely refined, U_{iso} parameters for C—H H atoms were refined, for CH_3 groups one common U_{iso} for each group was refined.
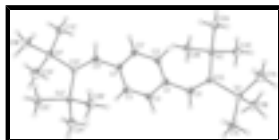
Figures

Fig. 1. A view of the molecule **1**. The displacement ellipsoids are drawn at 50% probability level, the hydrogen atoms are depicted as small spheres of arbitrary radii. [Symmetry code: (') $(3/2 - x, 1/2 - y, -z)$].
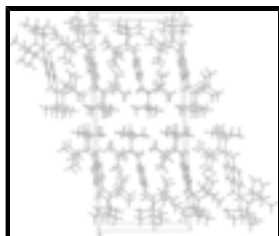

Fig. 2. Crystal packing of **1** as seen along [010] direction.

1,4-Bis[2,2-bis(trimethylsilyl)ethenyl]benzene

Crystal data

$C_{22}H_{42}Si_4$	$F_{000} = 920$
$M_r = 418.92$	$D_x = 1.034$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 6578 reflections
$a = 31.050$ (2) Å	$\theta = 2–29°$
$b = 6.5882$ (7) Å	$\mu = 0.23$ mm^{-1}
$c = 13.1661$ (14) Å	$T = 100$ (1) K
$\beta = 92.293$ (7)°	Needle, colourless
$V = 2691.2$ (4) Å^3	$0.5 \times 0.05 \times 0.05$ mm
$Z = 4$	

Data collection

Kuma KM-4-CCD four-circle diffractometer	3547 independent reflections
Radiation source: fine-focus sealed tube	2579 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
Detector resolution: 8.1929 pixels mm^{-1}	$\theta_{max} = 29.8°$
$T = 100(1)$ K	$\theta_{min} = 2.6°$
ω scan	$h = -41 \rightarrow 43$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	$k = -8 \rightarrow 9$

$T_{min} = 0.804$, $T_{max} = 0.989$

13212 measured reflections

$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.018$
3547 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.79450 (4)	0.2370 (2)	−0.01884 (9)	0.0181 (3)
C2	0.77151 (4)	0.0671 (2)	0.01147 (9)	0.0206 (3)
H2	0.7860 (4)	−0.065 (2)	0.0170 (10)	0.018 (3)*
C3	0.72761 (4)	0.0789 (2)	0.02898 (9)	0.0210 (3)
H3	0.7131 (5)	−0.043 (2)	0.0477 (12)	0.028 (4)*
C11	0.84141 (4)	0.2199 (2)	−0.03543 (9)	0.0199 (3)
H11	0.8558 (4)	0.144 (2)	0.0183 (10)	0.019 (3)*
C12	0.86443 (4)	0.29150 (19)	−0.11281 (9)	0.0175 (3)
Si1	0.924800 (11)	0.25655 (6)	−0.09758 (3)	0.02064 (10)
C1A	0.95192 (5)	0.5073 (3)	−0.11380 (15)	0.0386 (4)
H1A1	0.9816 (6)	0.485 (3)	−0.1030 (15)	0.056 (3)*
H1A2	0.9454 (6)	0.563 (3)	−0.1826 (16)	0.056 (3)*
H1A3	0.9424 (6)	0.602 (3)	−0.0683 (15)	0.056 (3)*
C1B	0.94583 (5)	0.0721 (3)	−0.19101 (12)	0.0312 (3)
H1B1	0.9482 (6)	0.128 (3)	−0.2592 (16)	0.054 (3)*

H1B2	0.9737 (6)	0.034 (3)	−0.1695 (14)	0.054 (3)*
H1B3	0.9279 (6)	−0.046 (3)	−0.1950 (15)	0.054 (3)*
C1C	0.94025 (5)	0.1578 (3)	0.03236 (12)	0.0325 (4)
H1C1	0.9299 (5)	0.023 (3)	0.0403 (14)	0.046 (3)*
H1C2	0.9694 (6)	0.151 (3)	0.0407 (13)	0.046 (3)*
H1C3	0.9291 (6)	0.245 (3)	0.0857 (15)	0.046 (3)*
Si2	0.839681 (11)	0.40940 (6)	−0.23262 (3)	0.01909 (10)
C2A	0.83715 (5)	0.6925 (2)	−0.22308 (13)	0.0302 (3)
H2A1	0.8175 (7)	0.738 (3)	−0.1752 (16)	0.062 (4)*
H2A2	0.8630 (7)	0.743 (3)	−0.2031 (16)	0.062 (4)*
H2A3	0.8276 (7)	0.750 (3)	−0.2808 (18)	0.062 (4)*
C2B	0.78577 (5)	0.2995 (2)	−0.26891 (11)	0.0245 (3)
H2B1	0.7631 (6)	0.338 (3)	−0.2245 (13)	0.046 (3)*
H2B2	0.7769 (5)	0.341 (3)	−0.3307 (14)	0.046 (3)*
H2B3	0.7883 (5)	0.160 (3)	−0.2726 (13)	0.046 (3)*
C2C	0.87442 (5)	0.3473 (3)	−0.34196 (11)	0.0315 (3)
H2C1	0.9030 (6)	0.400 (3)	−0.3346 (14)	0.044 (3)*
H2C2	0.8765 (5)	0.192 (3)	−0.3489 (13)	0.044 (3)*
H2C3	0.8622 (5)	0.404 (3)	−0.3989 (15)	0.044 (3)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0164 (6)	0.0255 (7)	0.0124 (5)	0.0011 (5)	0.0006 (4)	−0.0016 (5)
C2	0.0223 (7)	0.0216 (7)	0.0179 (6)	0.0049 (6)	0.0025 (5)	0.0013 (5)
C3	0.0212 (6)	0.0228 (7)	0.0193 (6)	−0.0007 (6)	0.0042 (5)	0.0001 (5)
C11	0.0176 (6)	0.0239 (8)	0.0182 (6)	0.0035 (5)	−0.0009 (5)	−0.0007 (5)
C12	0.0152 (6)	0.0175 (7)	0.0199 (6)	0.0010 (5)	0.0004 (4)	−0.0029 (5)
Si1	0.01415 (17)	0.0229 (2)	0.02477 (19)	0.00000 (14)	−0.00017 (13)	0.00310 (15)
C1A	0.0259 (8)	0.0347 (10)	0.0544 (11)	−0.0080 (7)	−0.0075 (7)	0.0049 (8)
C1B	0.0210 (7)	0.0345 (9)	0.0387 (8)	0.0073 (7)	0.0067 (6)	0.0015 (7)
C1C	0.0204 (7)	0.0448 (10)	0.0318 (8)	0.0042 (7)	−0.0035 (6)	0.0075 (7)
Si2	0.01679 (17)	0.0216 (2)	0.01887 (17)	0.00176 (14)	0.00090 (12)	0.00212 (14)
C2A	0.0252 (8)	0.0256 (8)	0.0395 (9)	0.0005 (6)	−0.0020 (6)	0.0056 (7)
C2B	0.0233 (7)	0.0291 (9)	0.0208 (7)	−0.0009 (6)	−0.0032 (5)	−0.0015 (6)
C2C	0.0291 (8)	0.0434 (10)	0.0222 (7)	0.0088 (7)	0.0049 (6)	0.0078 (7)

Geometric parameters (Å, °)

C1—C2	1.3944 (18)	C1B—H1B2	0.934 (19)
C1—C3[i]	1.3976 (18)	C1B—H1B3	0.96 (2)
C1—C11	1.4855 (17)	C1C—H1C1	0.954 (18)
C2—C3	1.3938 (17)	C1C—H1C2	0.907 (18)
C2—H2	0.982 (14)	C1C—H1C3	0.979 (19)
C3—C1[i]	1.3976 (18)	Si2—C2B	1.8683 (14)
C3—H3	0.957 (15)	Si2—C2A	1.8709 (17)
C11—C12	1.3527 (18)	Si2—C2C	1.8781 (15)
C11—H11	0.962 (14)	C2A—H2A1	0.94 (2)

C12—Si1	1.8914 (12)	C2A—H2A2	0.90 (2)
C12—Si2	1.8933 (13)	C2A—H2A3	0.89 (2)
Si1—C1B	1.8656 (16)	C2B—H2B1	0.966 (18)
Si1—C1A	1.8702 (18)	C2B—H2B2	0.891 (18)
Si1—C1C	1.8748 (15)	C2B—H2B3	0.922 (19)
C1A—H1A1	0.94 (2)	C2C—H2C1	0.953 (18)
C1A—H1A2	0.99 (2)	C2C—H2C2	1.030 (19)
C1A—H1A3	0.92 (2)	C2C—H2C3	0.907 (19)
C1B—H1B1	0.97 (2)		
C2—C1—C3^i	117.96 (11)	H1B2—C1B—H1B3	109.3 (17)
C2—C1—C11	119.81 (12)	Si1—C1C—H1C1	110.5 (11)
C3^i—C1—C11	122.18 (12)	Si1—C1C—H1C2	110.1 (11)
C1—C2—C3	121.19 (12)	H1C1—C1C—H1C2	106.3 (15)
C1—C2—H2	119.7 (8)	Si1—C1C—H1C3	111.5 (10)
C3—C2—H2	119.1 (8)	H1C1—C1C—H1C3	109.7 (15)
C2—C3—C1^i	120.83 (12)	H1C2—C1C—H1C3	108.6 (15)
C2—C3—H3	118.1 (9)	C2B—Si2—C2A	111.32 (7)
C1^i—C3—H3	121.1 (9)	C2B—Si2—C2C	104.82 (7)
C12—C11—C1	129.40 (12)	C2A—Si2—C2C	107.18 (8)
C12—C11—H11	119.5 (8)	C2B—Si2—C12	112.57 (6)
C1—C11—H11	111.1 (8)	C2A—Si2—C12	111.70 (7)
C11—C12—Si1	115.40 (9)	C2C—Si2—C12	108.84 (6)
C11—C12—Si2	124.17 (10)	Si2—C2A—H2A1	113.1 (11)
Si1—C12—Si2	120.38 (6)	Si2—C2A—H2A2	110.3 (12)
C1B—Si1—C1A	109.21 (8)	H2A1—C2A—H2A2	106.3 (17)
C1B—Si1—C1C	106.97 (8)	Si2—C2A—H2A3	112.5 (12)
C1A—Si1—C1C	108.11 (8)	H2A1—C2A—H2A3	103.5 (18)
C1B—Si1—C12	112.39 (6)	H2A2—C2A—H2A3	110.8 (18)
C1A—Si1—C12	109.22 (7)	Si2—C2B—H2B1	114.3 (10)
C1C—Si1—C12	110.82 (6)	Si2—C2B—H2B2	110.9 (11)
Si1—C1A—H1A1	106.8 (11)	H2B1—C2B—H2B2	105.4 (14)
Si1—C1A—H1A2	110.7 (11)	Si2—C2B—H2B3	108.7 (11)
H1A1—C1A—H1A2	111.1 (16)	H2B1—C2B—H2B3	111.0 (15)
Si1—C1A—H1A3	111.5 (12)	H2B2—C2B—H2B3	106.3 (16)
H1A1—C1A—H1A3	110.2 (16)	Si2—C2C—H2C1	113.8 (11)
H1A2—C1A—H1A3	106.6 (16)	Si2—C2C—H2C2	108.9 (9)
Si1—C1B—H1B1	113.9 (11)	H2C1—C2C—H2C2	108.0 (14)
Si1—C1B—H1B2	108.6 (11)	Si2—C2C—H2C3	108.1 (11)
H1B1—C1B—H1B2	106.0 (15)	H2C1—C2C—H2C3	107.0 (15)
Si1—C1B—H1B3	110.3 (11)	H2C2—C2C—H2C3	111.2 (15)
H1B1—C1B—H1B3	108.7 (16)		
C3^i—C1—C2—C3	1.42 (19)	Si2—C12—Si1—C1A	56.09 (10)
C11—C1—C2—C3	179.12 (11)	C11—C12—Si1—C1C	−7.46 (13)
C1—C2—C3—C1^i	−1.5 (2)	Si2—C12—Si1—C1C	175.09 (8)
C2—C1—C11—C12	134.75 (15)	C11—C12—Si2—C2B	−31.27 (13)
C3^i—C1—C11—C12	−47.6 (2)	Si1—C12—Si2—C2B	145.95 (8)
C1—C11—C12—Si1	174.44 (11)	C11—C12—Si2—C2A	94.83 (12)

C1—C11—C12—Si2	−8.2 (2)	Si1—C12—Si2—C2A	−87.95 (9)
C11—C12—Si1—C1B	112.18 (11)	C11—C12—Si2—C2C	−147.03 (12)
Si2—C12—Si1—C1B	−65.27 (10)	Si1—C12—Si2—C2C	30.19 (10)
C11—C12—Si1—C1A	−126.46 (11)		

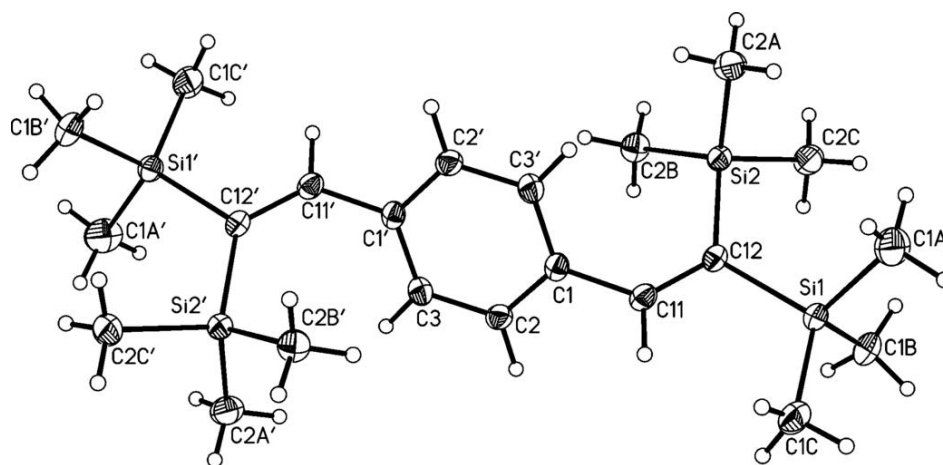Symmetry codes: (i) $-x+3/2, -y+1/2, -z$.

Fig. 1

Fig. 2