

RefinementRefinement on F^2 Final $R = 0.047$ $wR = 0.056$ $S = 1.61$

1184 reflections

118 parameters

H-atom parameters not refined

 $w = 4F_o^2/\sigma^2(F_o)^2$ $(\Delta/\sigma)_{\max} = 0.01$ $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$ Atomic scattering factors
from *International Tables
for X-ray Crystallography* (1974, Vol. IV, Table
2.2A)Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j.$$

	x	y	z	B_{eq}
Cl(1)	0.9171 (2)	0.13564 (7)	0.8161 (1)	3.88 (4)
N(2)	0.0287 (4)	0.4194 (2)	0.1857 (3)	2.5 (1)
N(3)	0.0725 (5)	0.4496 (2)	0.3277 (3)	2.7 (1)
N(4)	-0.0241 (5)	0.3150 (2)	-0.0009 (3)	2.9 (1)
N(5)	-0.0545 (5)	0.3889 (2)	-0.1023 (3)	3.3 (1)
C(1)	0.0160 (5)	0.3322 (2)	0.1402 (4)	2.2 (1)
C(4)	0.1020 (5)	0.3856 (2)	0.4267 (4)	2.4 (1)
C(5)	0.1244 (6)	0.2233 (3)	0.5072 (4)	2.7 (1)
C(6)	0.1141 (6)	0.1313 (3)	0.4725 (4)	2.9 (1)
C(7)	0.0735 (6)	0.1026 (2)	0.3258 (4)	2.7 (1)
C(8)	0.0402 (5)	0.1668 (2)	0.2143 (4)	2.5 (1)
C(9)	0.0487 (5)	0.2603 (2)	0.2492 (4)	2.0 (1)
C(10)	0.0925 (5)	0.2889 (2)	0.3951 (3)	2.1 (1)

Table 2. Bond lengths (\AA) and angles ($^\circ$) between non-H atoms and hydrogen-bond geometry (\AA , $^\circ$)

N(2)—N(3)	1.371 (4)	C(5)—C(6)	1.374 (5)
N(2)—C(1)	1.334 (4)	C(5)—C(10)	1.400 (5)
N(3)—C(4)	1.299 (4)	C(6)—C(7)	1.406 (5)
N(4)—N(5)	1.420 (4)	C(7)—C(8)	1.383 (5)
N(4)—C(1)	1.316 (4)	C(8)—C(9)	1.396 (5)
C(1)—C(9)	1.444 (4)	C(9)—C(10)	1.398 (4)
C(4)—C(10)	1.435 (4)		
N(3)—N(2)—C(1)	126.9 (3)	C(6)—C(7)—C(8)	120.3 (3)
N(2)—N(3)—C(4)	115.5 (3)	C(7)—C(8)—C(9)	119.2 (3)
N(5)—N(4)—C(1)	119.8 (3)	C(1)—C(9)—C(8)	123.1 (3)
N(2)—C(1)—N(4)	119.2 (3)	C(1)—C(9)—C(10)	116.4 (3)
N(2)—C(1)—C(9)	118.1 (3)	C(8)—C(9)—C(10)	120.5 (3)
N(4)—C(1)—C(9)	122.7 (3)	C(4)—C(10)—C(5)	121.2 (3)
N(3)—C(4)—C(10)	124.1 (3)	C(4)—C(10)—C(9)	118.9 (3)
C(6)—C(5)—C(10)	119.5 (3)	C(5)—C(10)—C(9)	119.9 (3)
C(5)—C(6)—C(7)	120.6 (3)		
X—H...Y	X...Y	H...Y	X—H...Y
N(4)—H(4A)...Cl(1 ⁱ)	3.098 (3)	2.122 (1)	173.1 (2)
N(2)—H(2)...N(5 ⁱⁱ)	2.910 (4)	2.143 (3)	134.6 (2)

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x, 1 - y, -z$.

Data collection and cell refinement: *Rigaku MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1988). Programs used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). All calculations including data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Data were collected using a scan rate of $32^\circ \text{ min}^{-1}$ in ω and a scan width of $(1.47 + 0.30\tan\theta)^\circ$. The ratio of peak counting time to background counting time was 2:1. Refinement was by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms. The coordinates of the H atoms were determined from difference Fourier synthesis but the H-atom parameters were not included in the refinement.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71254 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1021]

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Acta Cryst. (1993). **C49**, 1845–1848**Structure of Cyclo-1,1',4,4'-bis(1,1,3,3-tetramethyl-1,3-disiloxanediy) dibenzene**KHALIL A. ABBOUD,* DENNIS W. SMITH JR
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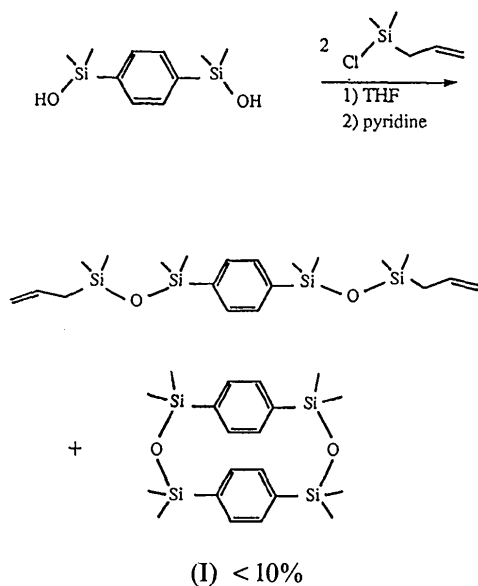
Abstract

The structure of 2,2,4,4,9,9,11,11-octamethyl-3,10-dioxa-2,4,9,11-tetrasilatricyclo[10.2.2.2^{5,8}]octadeca-1(14),5,7,12,15,17-hexaene (I) consists of molecules located on crystallographic centers of inversion (half a molecule in the asymmetric unit). The two phenyl rings are parallel to each other with a separation of 3.63 \AA . The title compound (I) has been considered as a monomer for catalytic ring-opening polymerization. It was synthesized, using allyl(chloro)dimethylsilane, by the condensation of bis(hydroxydimethylsilyl)benzene.

Comment

Carbosiloxanes are important compounds when considering their use as monomers in polymer chemistry (Mark, 1990). Considerable emphasis has been given to the synthesis of polysilylene-siloxanes (Dvornic & Lenz, 1992) by employing the condensation polymerization of linear hydroxy- and halo- terminated silicon monomers. In particular, cyclocarbosiloxanes have been polymerized by ring-opening techniques in order to obtain a variety of polycarbosiloxanes (Nametkin, Islamov, Gusel'nikov & Vdovin, 1992).

In our continuing studies to develop silicon-containing monomers for acyclic diene metathesis (ADMET) polymerization (Wagener & Smith, 1991), we have explored the condensation of bis(hydroxydimethylsilyl)benzene with allyl(chloro)dimethylsilane. This reaction gave the bis(allyldisiloxanyl)benzene monomer and the crystalline cyclic siloxane (I). Compound (I) has been sought previously (Merker & Scott, 1964) for catalytic ring-opening polymerization, albeit with little success. Only a melting point has been given previously for (I) (Merker & Scott, 1964).



A thermal ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the molecule with the atom-labeling scheme is given in Fig. 1. The structure is discussed in comparison with three closely related structures: *p*-bis(hydroxydimethylsilyl)benzene (II) (Alexander, Northolt & Engmann, 1967), 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasilol[2.2]-paracyclophane (III) (Sakurai, Hoshi, Kamiya, Hosomi & Kabuto, 1986) and *p*-bis(tetramethylsilyl)benzene (IV) (Menczel & Kiss, 1975). The Si to the phenyl-ring C bonds are in good agreement with

their counterparts in (II), (III) and (IV). The only distortion in the phenyl ring as a result of its substituents is exhibited by the deviation of angles C2—C1—C6 and C3—C4—C5 from the 120° ideal benzene ring angle, a feature also observed in (II), (III) and (IV). The Si—O bond distances are shorter than those observed in (II) (an average of 1.647 Å in three independent molecules), and in octamethylcyclotetrasiloxane (V) [four independent bonds that range from 1.628 to 1.652 Å (Steinfink, Post & Fankuchen, 1955)]. The Si atoms are slightly displaced from the plane of the phenyl ring (5.9° for both Si and Si') compared to a displacement of 15° in (III). C1 and C4 are in the plane of the phenyl ring while their counterparts in (III) are displaced by an angle of 4.3°. The smaller displacement observed in (I) compared to (III) results from the presence of the bridging O atom in (I), which has an angle of 156.0(2)° between the Si atoms. The opening of the O angle, which is larger than that observed in (V) (142.6°), minimizes repulsion between the π -electron clouds without large displacements of the Si atoms from the planes of the phenyl rings.

Compound (I) crystallized directly from the product mixture upon heating at 323 K and under a vacuum of 10^{-6} mmHg (1 mmHg = 133.322 Pa). The crystals were washed with ethanol and vacuum dried; m.p. = 481 K (literature 481 K). ^1H NMR 200 MHz and ^{13}C NMR 50 MHz spectra were obtained with a Varian XL-Series NMR superconducting spectrometer system. Chloroform-*d* was used as solvent and chemical shifts reported for ^1H and ^{13}C NMR were internally referenced to tetramethylsilane. ^1H NMR (200 MHz, CDCl_3): δ 0.39 (s, 12 H), 7.0 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, CDCl_3): δ 0.08, 132.15 (aromatic CH), 138.71 (*ipso*). High-resolution mass spectroscopy (HRMS) data were obtained with a Finnigan 4500 gas chromatograph-mass spectrometer. HRMS (CI): m/z , 416.1485; calculated for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}_4$, 416.1480.

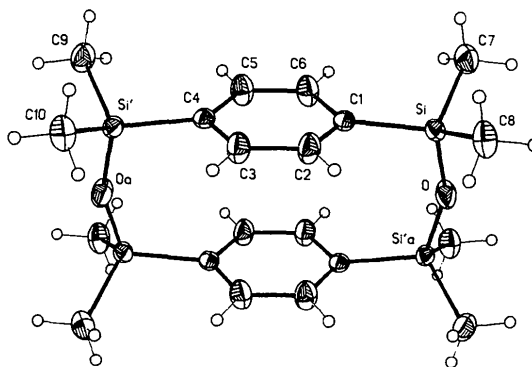


Fig. 1. Molecular structure of (I), with 50% probability ellipsoids, showing the atom-numbering scheme.

Experimental

Crystal data

C₂₀H₃₂O₂Si₄M_r = 416.8

Triclinic

P $\bar{1}$

a = 6.616 (1) Å

b = 8.661 (1) Å

c = 11.693 (1) Å

 α = 77.79 (1)° β = 87.14 (1)° γ = 69.02 (1)°V = 611.2 (1) Å³

Z = 1

D_x = 1.132 Mg m⁻³Mo K α radiation λ = 0.71073 Å

Cell parameters from 50 reflections

 θ = 20–22° μ = 0.25 mm⁻¹

T = 293 K

Plates

0.42 × 0.30 × 0.15 mm

Colorless

Data collection

Siemens P3mV diffractometer

 ω scans

Absorption correction: analytical

T_{min} = 0.851, T_{max} = 0.973

3102 measured reflections

2837 independent reflections

2041 observed reflections

[F > 6 σ (F)]R_{int} = 0.0134 θ_{\max} = 27.5°

h = 0 → 8

k = -11 → 11

l = -15 → 15

4 standard reflections

monitored every 96

reflections

intensity variation: 1%

Refinement

Refinement on F

Final R = 0.0516

wR = 0.0655

S = 2.25

2041 reflections

170 parameters

All H-atom parameters refined

w = 1/[$\sigma^2(F) + 0.0004F$]² $(\Delta/\sigma)_{\max}$ = 0.001 $\Delta\rho_{\max}$ = 0.35 e Å⁻³ $\Delta\rho_{\min}$ = -0.29 e Å⁻³

Atomic scattering factors

from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

C1—Si—C8		110.9 (2)
C7—Si—C8	1.853 (4)	110.0 (2)
C8—Si—O	1.836 (5)	108.5 (2)
Oa*—Si'—C4	1.618 (2)	108.40 (13)
Oa—Si'—C9		108.9 (2)
C4—Si'—C9	1.874 (3)	111.1 (2)
C4—Si'—C10		110.7 (2)
C9—Si'—C10	1.839 (4)	109.5 (2)
C10—Si'—Oa*	1.833 (5)	108.1 (2)
Si—O—Si'a*		156.0 (2)
C2—C1—C6		115.7 (3)
C5—C4—C3		115.7 (3)

* Si'a and Oa are symmetry equivalents of Si' and O, respectively, related by a center of inversion.

The ω -scan width was symmetrical over 1.2% about the K $\alpha_{1,2}$ maximum and the background was offset 1.0 and -1.0 (in ω) from the K $\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min⁻¹ (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV). Anomalous-dispersion corrections were from Cromer & Liberman (1970). All H atoms were freely refined with the temperature factors of the methyl H atoms fixed at 0.10 Å. Programs used: *SHELXTL-Plus* (Sheldrick, 1990) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics; *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least squares); *FUER* (S. B. Larson, personal communication) for geometric and parameter tables.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71151 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1046]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
Si	0.43516 (14)	0.13160 (9)	0.18326 (6)	0.0522 (4)
Si'	0.55715 (13)	0.23819 (9)	0.71208 (6)	0.0492 (3)
O	0.4279 (5)	-0.0568 (3)	0.2087 (2)	0.093 (2)
C1	0.4702 (5)	0.1857 (3)	0.3264 (2)	0.0472 (11)
C2	0.6705 (6)	0.1537 (5)	0.3742 (3)	0.071 (2)
C3	0.6976 (6)	0.1753 (5)	0.4858 (3)	0.0705 (15)
C4	0.5227 (4)	0.2340 (3)	0.5548 (2)	0.0465 (10)
C5	0.3222 (6)	0.2727 (5)	0.5045 (3)	0.072 (2)
C6	0.2961 (6)	0.2498 (5)	0.3939 (3)	0.073 (2)
C7	0.1766 (7)	0.2806 (6)	0.1094 (3)	0.087 (2)
C8	0.6624 (8)	0.1365 (6)	0.0876 (3)	0.087 (2)
C9	0.3265 (7)	0.4044 (5)	0.7591 (4)	0.079 (2)
C10	0.8086 (7)	0.2721 (6)	0.7358 (4)	0.081 (2)

Table 2. A selected set of bond lengths (Å) and angles (°) for the non-H atoms of compound (I)

A—B—C	A—B	A—B—C
O—Si—C1	1.613 (3)	108.67 (12)
O—Si—C7		108.5 (2)
C1—Si—C7	1.877 (3)	110.2 (2)

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Structure of a Phosphazene–Aniline Compound

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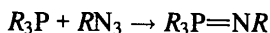
(Received 21 October 1992; accepted 3 March 1993)

Abstract

The title compound [bis(trimethylphosphine phenylimide)–bis(aniline) (I), a 1:1 ratio of phosphazene and aniline molecules] was synthesized from the trapping of an *in situ* palladium nitrene complex with trimethylphosphine. Crystals of (I) consist of tetramers (two phosphazene and two aniline molecules) located at the $0,0,\frac{1}{2}$ center of inversion in the space group $P\bar{1}$. The N atoms of the phosphazene molecules are involved in bifurcated hydrogen bonds with the amino H atoms of the aniline molecules.

Comment

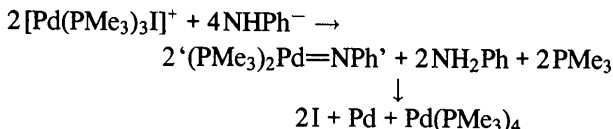
Tertiary alkyl and aryl phosphines have frequently been employed as trapping reagents for the isolation of reactive compounds and intermediates. One such family of compounds that is a product of these trapping reactions is phosphazenes. Phosphazenes are the nitrogen analogues of phosphorous ylides $R_3P=CR_2$. To produce a phosphazene from a tertiary phosphine, a nitrene source is required to generate the $P=N$ double bond (Staudinger & Hauser, 1921):



Recently it was demonstrated that the phosphazene complex $Ph_3P=NPh$ was isolated from a zero-valent tungsten nitrene complex in the presence

of PPh_3 (Sleiman, Mercer & McElwee-White, 1989).

Our interests involve the synthesis and characterization of nitrene complexes of palladium. When two equivalents of KNHPh were added to a solution of $[Pd(PMe_3)_3I][BFD_4]$ in THF at 195 K, compound (I) was isolated. Compound (I) was crystallized in pentane at 273 K, affording highly air and water sensitive light-brown needles of the title compound. It is likely that the generation of an *in situ* palladium nitrene complex in the presence of free PMe_3 is responsible for the formation of (I):



Aniline is a by-product of the deprotonation of the second equivalent of KNHPh used to generate the intermediate nitrene complex. A Pd^0 species in the form of $Pd(PMe_3)_4$ was also produced in the reaction.

The thermal ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the tetramer (two asymmetric units) with the atom-labeling scheme is given in Fig. 1. The tetramers are formed by hydrogen bonding between the amino H atoms and the N atoms of the phosphazene molecules. The hydrogen bonds have the following parameters: $N11-H11a = 0.83$ (3), $H11a \cdots N1a$ (related to N1 by the symmetry operation $-x, -y, 1-z$) = 2.34 (3), $N11 \cdots N1a = 3.152$ (4) Å, $N11-H11a \cdots N1a = 166$ (4)°, $N11-H11b = 0.90$ (4), $H11b \cdots N1 = 2.20$ (4), $N11 \cdots N1 = 3.092$ (4) Å, $N11-H11b \cdots N1 = 174$ (4)°.

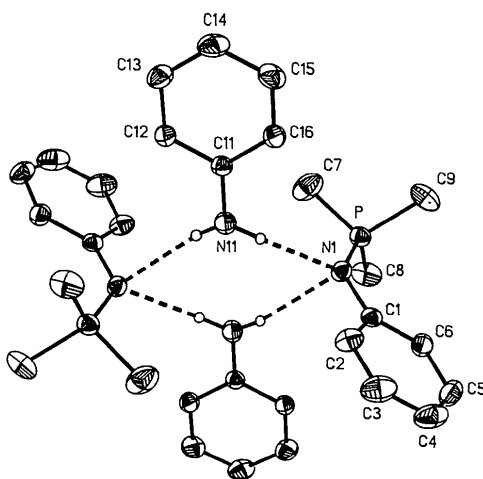


Fig. 1. Thermal ellipsoid drawing of two asymmetric units showing the tetramer, two phosphazene and two aniline molecules, held together by hydrogen bonding. Only the amino H atoms are included in the drawing. 50% probability ellipsoids are shown as well as the atom labels of the asymmetric unit.