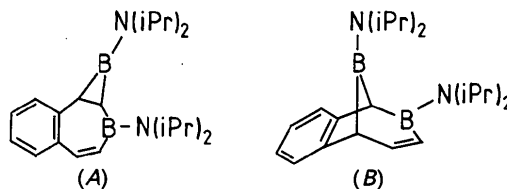


Fig. 1. The molecular structure of C<sub>22</sub>H<sub>36</sub>B<sub>2</sub>N<sub>2</sub>.

ano-2*H*-benzo[*c*]borepine (*B*) (Meller, Bromm, Maringgele, Böhler & Elter, 1988).



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aromatic compounds a product, C<sub>10</sub>H<sub>8</sub>.2BN(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>, was obtained with naphthalene. It was not possible to determine by NMR (H, B, C, N) and mass spectrometry whether the structure of this product was that of 1,2-bis(diisopropylamino)-1,1a,2,8b-tetrahydroborireno[2,3-*b*][3]benzoborepine (*A*) or 2,10-bis(diisopropylamino)-1,5-dihydro-1,5-epibor-

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## Structures of Solvated Hexaphenyldisiloxanes

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**Abstract.** C<sub>36</sub>H<sub>30</sub>OSi<sub>2</sub>.2C<sub>6</sub>H<sub>6</sub> (1); *M<sub>r</sub>* = 691.03, trigonal, space group *R*3̄, *a<sub>H</sub>* = 11.325 (4), *c<sub>H</sub>* = 26.738 (6) Å [*a<sub>R</sub>* = 11.054 (2) Å, *α<sub>R</sub>* = 61.63 (2)°], *V* = 2969.86 Å<sup>3</sup>, *Z* = 3, *D<sub>x</sub>* = 1.159 g cm<sup>-3</sup>, *μ* = 0.93 cm<sup>-1</sup>, λ(Mo *Kα*) = 0.71069 Å, *F*(000) = 1098, *T* = 293 K, final *R* = 0.044 for 1293 observed reflections with *I* > 3σ(*I*). C<sub>36</sub>H<sub>30</sub>OSi<sub>2</sub>.2C<sub>7</sub>H<sub>8</sub> (2); *M<sub>r</sub>* = 719.08, trigonal, space group *R*3̄, *a<sub>H</sub>* = 11.542 (4), *c<sub>H</sub>* = 26.735 (6) Å [*a<sub>R</sub>* = 11.129 (2) Å, *α<sub>R</sub>* = 62.47 (2)°], *V* = 3084.41 Å<sup>3</sup>, *Z* = 3, *D<sub>x</sub>* = 1.161 g cm<sup>-3</sup>, *μ* = 0.91 cm<sup>-1</sup>, λ(Mo *Kα*) = 0.71069 Å, *F*(000) = 1146, *T* = 293 K, final *R* = 0.066 for 727 observed reflections with *I* > 3σ(*I*). (1) and (2) are isotypic. The molecule has 3̄ symmetry with the phenyl groups in staggered

conformation. It consists of a central fragment Si—O—Si along the crystallographic *c* axis being linear by an inversion center. The principal interatomic distances are *d*(Si—O) = 1.622 (1) and *d*(Si—C) = 1.899 (2) Å in (1), and *d*(Si—O) = 1.620 (2) and *d*(Si—C) = 1.866 (6) Å in (2). In (1) the anisotropic thermal displacement parameters for the O atom, however, indicate a deviation from the linearity of the Si—O—Si fragment caused by static or dynamic disorder. This deviation would yield *d*(Si—O) = 1.64 Å and β(Si—O—Si) = 163°.

**Experimental.** [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>O.2C<sub>6</sub>H<sub>6</sub> (1) and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>O.2C<sub>7</sub>H<sub>8</sub> (2): colourless crystals of dimensions 0.1 × 0.1 × 0.2 mm and 0.1 × 0.1 × 0.15 mm. Diffraction maxima with 2θ ≤ 55° were collected on a computer-controlled four-circle Syntex P1 diffrac-

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Table 1. Refined atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for (1) and (2) with e.s.d.'s in parentheses

	x	y	z	$U_{\text{eq}}^*$
(1)				
Si	0	0	0.06066 (3)	414 (2)
O	0	0	0	520 (9)
C1	0.1221 (2)	0.1762 (2)	0.08272 (6)	460 (8)
C2	0.1935 (2)	0.2008 (2)	0.12748 (7)	563 (10)
C3	0.2844 (2)	0.3325 (2)	0.14309 (8)	643 (11)
C4	0.3061 (2)	0.4415 (2)	0.11414 (9)	664 (11)
C5	0.2367 (3)	0.4207 (2)	0.07016 (9)	706 (11)
C6	0.1448 (2)	0.2889 (2)	0.05456 (8)	605 (10)
C7	0.1315 (6)	0.0347 (12)	0.2700 (2)	1510 (35)
C8	0.0974 (10)	0.1303 (6)	0.2700 (2)	1546 (47)
H2	0.1786 (26)	0.1267 (27)	0.1479 (10)	700
H3	0.3311 (28)	0.3443 (27)	0.1734 (10)	700
H4	0.3685 (28)	0.5276 (28)	0.1238 (10)	700
H5	0.2519 (27)	0.4907 (27)	0.0483 (10)	700
H6	0.0995 (27)	0.2810 (27)	0.0238 (10)	700
H7	0.2196 (51)	0.0619 (52)	0.2708 (17)	1600
H8	0.1474 (50)	0.2183 (50)	0.2732 (17)	1600
(2)				
Si	0	0	0.06066 (8)	422 (7)
O	0	0	0	500 (21)
C1	0.0547 (7)	0.1731 (5)	0.0827 (2)	472 (24)
C2	0.0078 (6)	0.1975 (7)	0.1276 (2)	675 (33)
C3	0.0507 (7)	0.3279 (7)	0.1431 (2)	739 (36)
C4	0.1398 (7)	0.4349 (7)	0.1149 (2)	720 (35)
C5	0.1879 (7)	0.4139 (6)	0.0711 (2)	753 (35)
C6	0.1455 (6)	0.2828 (6)	0.0553 (2)	670 (32)
C7	-0.1109 (42)	0.0246 (52)	0.2730 (7)	2706 (423)
C8	0.0078 (68)	0.1139 (60)	0.2728 (8)	2282 (385)
C9	0.0468 (63)	0.2321 (36)	0.2810 (18)	1698 (368)
H2	-0.0351 (66)	0.1224 (66)	0.1509 (22)	700
H3	0.0269 (65)	0.3429 (66)	0.1748 (25)	700
H4	0.1664 (64)	0.5296 (66)	0.1267 (22)	700
H5	0.2651 (64)	0.4946 (64)	0.0464 (23)	700
H6	0.1715 (62)	0.2582 (63)	0.0207 (22)	700
H7	-0.1905 (131)	-0.0251 (159)	0.2821 (45)	1500
H8	0.1454 (451)	0.1406 (298)	0.2541 (77)	1500

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

tometer, using graphite-monochromated Mo  $K\alpha$  radiation and  $\omega$ -scan mode; cell parameters by least squares from 15 centered reflections  $4 < 2\theta < 27^\circ$ ; data collection of (1) 2576 and (2) 3202 unique [ $R_{\text{int}} = 0.021$  (1) and  $0.035$  (2)] reflections of which 1293 and 727 were treated as observed with  $I \geq 3\sigma(I)$ ; empirical absorption correction based on  $\psi$  scan of 7 and 6 reflections; range of  $hkl$  (1):  $h = 0 \rightarrow 14$ ,  $k = 0 \rightarrow 13$  and  $l = -11 \rightarrow 13$ . Range of  $hkl$  (2):  $h = -13 \rightarrow 14$ ,  $k = 0 \rightarrow 14$  and  $l = 0 \rightarrow 34$ . The structures were solved by direct method and refined on  $F$  by block diagonal matrix least-squares minimized  $w(\Delta F)^2$  with program system *SHELX* (Sheldrick, 1976). H-atom positions located by difference Fourier synthesis (H2–H6) and calculated (H7, H8), respectively. In  $[(C_6H_5)_3Si]_2O \cdot 2C_7H_8$  the site occupancy factor of C9 was fixed at 1/3, as the methyl group of toluene is positionally disordered. The  $U$  values for the H atoms were kept fixed. Positional and displacement parameters of all atoms except H were refined anisotropically, the large values of the displacement parameters of C7 and C8 of (1) and of C7, C8 and C9 of (2) suggest a rotational disorder of the solvent molecules. In (1) the larger  $U_{11}$  value of the O atom

Table 2.  $[(C_6H_5)_3Si]_2O \cdot 2C_6H_6$  Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (1) and (2) with e.s.d.'s in parentheses

(1)					
Si—O	1.622 (1)	C4—C5	1.372 (4)		
Si—C1	1.899 (2)	C5—C6	1.410 (4)		
C1—C2	1.398 (3)	C6—C1	1.408 (2)		
C2—C3	1.406 (4)	C7—C8*	1.356 (12)		
C3—C4	1.384 (3)	C8—C7	1.340 (20)		
O—Si—C1	108.1 (1)	Si—O—Si*	180		
C1—Si—C1*	110.8 (1)	C2—C1—C6	116.6 (2)		
(2)					
Si—O	1.620 (2)	C4—C5	1.368 (9)	C7—C8*	1.24 (7)
Si—C1	1.866 (6)	C5—C6	1.403 (9)	C8—C7	1.49 (11)
C1—C2	1.400 (9)	C6—C1	1.384 (7)	C8—C9	1.22 (8)
C2—C3	1.392 (11)				
C3—C4	1.372 (8)				
O—Si—C1	108.5 (2)	Si—O—Si*	180		
C1—Si—C1*	110.4 (2)	C2—C1—C6	117.6 (6)		

\* Atom related by symmetry

Table 3. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ ) for (1) and (2) with e.s.d.'s in parentheses

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
(1)						
Si	447 (3)	$U_{11}$	348 (4)	0	0	$1/2 U_{11}$
O	603 (12)	$U_{11}$	353 (15)	0	0	$1/2 U_{11}$
C1	489 (10)	482 (10)	428 (9)	50 (7)	28 (7)	258 (9)
C2	576 (12)	597 (12)	512 (11)	-27 (9)	41 (9)	291 (10)
C3	669 (14)	696 (14)	609 (12)	24 (11)	176 (11)	374 (12)
C4	522 (13)	760 (15)	726 (14)	134 (12)	155 (11)	332 (12)
C5	486 (12)	799 (16)	668 (14)	3 (12)	-25 (10)	199 (11)
C6	542 (12)	680 (14)	506 (11)	-45 (10)	36 (9)	240 (10)
C7	1617 (52)	1189 (41)	962 (27)	-70 (26)	-391 (36)	129 (38)
C8	2518 (72)	1628 (53)	1020 (29)	-432 (38)	-326 (49)	1434 (53)
(2)						
Si	432 (9)	$U_{11}$	402 (11)	0	0	$1/2 U_{11}$
O	500 (24)	$U_{11}$	454 (42)	0	0	$1/2 U_{11}$
C1	465 (30)	470 (30)	505 (27)	-11 (22)	-36 (21)	253 (26)
C2	757 (42)	677 (43)	606 (33)	-78 (29)	53 (30)	370 (37)
C3	812 (45)	760 (47)	703 (37)	-171 (35)	-2 (34)	437 (39)
C4	822 (47)	545 (39)	860 (43)	-136 (33)	-162 (36)	392 (38)
C5	846 (49)	544 (39)	719 (38)	11 (30)	11 (34)	235 (36)
C6	763 (43)	600 (39)	596 (32)	-39 (29)	7 (29)	303 (34)
C7	1972 (22)	5564 (849)	795 (95)	-567 (198)	-204 (135)	2044 (360)
C8	2826 (400)	4315 (586)	1042 (115)	-399 (206)	-380 (193)	2788 (489)
C9	2680 (626)	968 (271)	1769 (350)	218 (254)	927 (378)	1155 (391)

The anisotropic displacement exponent takes the form:  
 $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}\dots)$

as compared to  $U_{33}$  indicates a static or dynamic disorder. Taking  $\bar{u} = 0.246 \text{\AA}$  as a measure for the displacement in the  $ab$  plane, the corrected ( $\star$ ) values are  $d^*(\text{Si—O}) = 1.64 \text{\AA}$  and  $\beta^*(\text{Si—O—Si}) = 163^\circ$ . However, no indication for an ordering of the bent Si—O—Si fragment could be found at room temperature. (1): 153 parameters were varied in total, overdetermination ratio 8.5, refinement converged to  $R = 0.044$ ,  $S = 1.291$ , unit weights. Final  $(\Delta/\sigma)_{\text{max}} = 0.006$ ,  $\Delta\rho_{\text{max}} = 0.26$  and  $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$  on final difference Fourier map. (2): 117 parameters were varied in total, overdetermination ratio 6.2, refinement to  $R = 0.066$ , unit weights. Final  $(\Delta/\sigma)_{\text{max}} = 0.010$ ,  $\Delta\rho_{\text{max}} = 0.40$  and  $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$  on

final difference Fourier map. Atomic scattering factors taken as in the *SHELX* program. The atomic coordinates, interatomic distances and angles as well as thermal displacement parameters are given in Tables 1, 2 and 3, respectively. The molecule and the atom labeling are shown in Fig. 1\* and a stereoview of (1) in Fig. 2.

**Related literature.** The isosteric structure of unsolvated  $(Ph_3Si)_2O$  was determined by Glidewell &

\* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53043 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

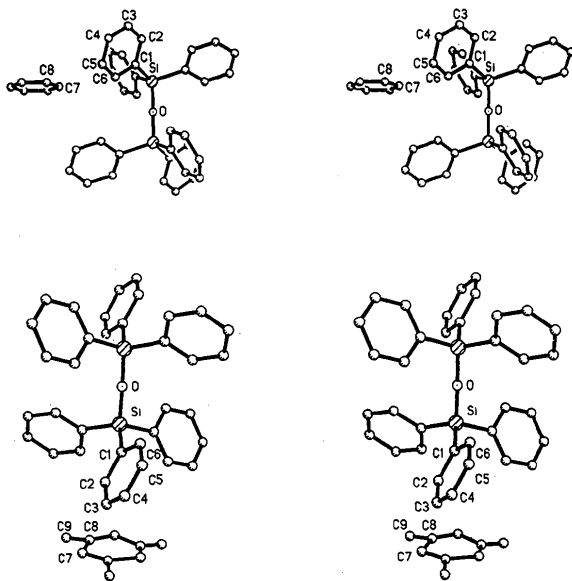


Fig. 1. Stereoviews of  $[(C_6H_5)_3Si]_2O \cdot 2C_6H_6$  (1) (top) and  $[(C_6H_5)_3Si]_2O \cdot 2C_7H_8$  (2) (bottom) with the atoms labeled as given in the tables.

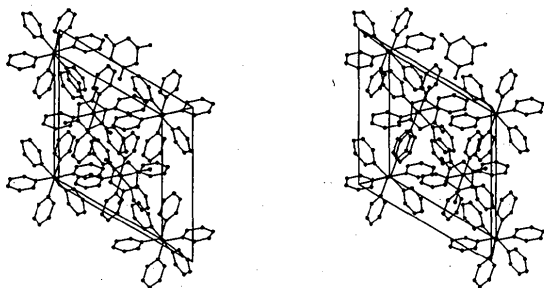


Fig. 2. Stereoview of  $[(C_6H_5)_3Si]_2O \cdot 2C_7H_8$ . Some molecules generated by translation have been omitted for the purpose of clarity.

Table 4. Lattice constants of (1) ( $cm^3 mol^{-1}$ ),  $a$  and  $c$  in Å

$a$	$c$	$U$	
11.196 (4)	26.515 (15)	577.8	Suwinska, Palenik & Gerdil (1986)
11.325 (4)	26.738 (6)	595.7	This work
11.5378 (5)	26.7717 (4)	618.4	Dubchak, Shklover & Struchkov (1983)

Liles (1978), two earlier structure determinations of the benzene solvate have been reported by Suwinska, Palenik & Gerdil (1986) and Dubchak, Shklover & Struchkov (1983). The lattice constants of  $[(C_6H_5)_3Si]_2O \cdot 2C_6H_6$  (1) differ markedly (see Table 4).

Taking  $U$  from the solvent free siloxane ( $454.3 \text{ \AA}^3 \text{ mol}^{-1}$ ), one should expect for a disolvate from the molar volume of benzene  $U = 75.3 \text{ cm}^3 \text{ mol}^{-1}$  a total volume of  $604.9 \text{ cm}^3 \text{ mol}^{-1}$ . We note that the volume for  $[(C_6H_5)_3Si]_2O \cdot 2C_6H_6$  of Dubchak, Shklover & Struchkov is greater than that of  $[(C_6H_5)_3Si]_2O \cdot 2C_7H_8$  ( $619.3 \text{ cm}^3 \text{ mol}^{-1}$ ). Based on their relatively high  $R$  value it seems likely that they indeed have dealt with the  $[(C_6H_5)_3Si]_2O \cdot 2C_7H_8$  compound. The smaller volume of (1) as compared to the calculated value indicates a variable concentration of benzene, which could not be verified here by refining the site occupancy factors of C7 and C8. The crystal structures of several related compounds have been reported. For  $Ph_3SiOSiPh_2H$ , see Wojnowski, Becker, Peters, Peters & von Schnering (1988a); for  $(Ph_2HSi)_2O$ , see Wojnowski, Peters, Peters, Meyer & von Schnering (1986); for  $(Ph_2MeSi)_2O$ , see Wojnowski, Becker, Peters, Peters & von Schnering (1988b); for a complete discussion of the crystal structures of compounds of this type see Wiberg, Kühnel, Schurz, Borrmann & Simon (1988); also the discussion of Karle, Karle & Nielsen (1986) and Liebau (1985).

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