Références

DUBOST, J. P. (1978). Thèse Doctorat ès Sciences Pharmaceutiques. Univ. de Bordeaux II.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274–285.

LÉGER, J. M. (1979). Thèse Doctorat ès Sciences Physiques. Univ. de Bordeaux I.

TALUKDAR, A. N. & CHAUDHURI, B. (1976). *Acta Cryst.* B**32**, 803–808.

THEWALT, U. & BUGG, C. E. (1972). *Acta Cryst.* B**28**, 82–92.

Acta Cryst. (1981). B**37**, 754–756

The Structure of 1,1,1,3,3,3-Hexaphenyldisilazane

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Abstract. $C_{36}H_{31}NSi_2$, orthorhombic, $P2_12_12_1$, a = 20·072 (6), b = 13·317 (8), c = 11·249 (17) Å; M_r = 533·82, D_c = 1·179 Mg m^{-3}, Z = 4; μ(Mo $K\alpha$) = 0·106 mm^{-1}. Final R is 0·0774. The Si—N—Si angle is 138·1 (4)°, the mean Si—N distance 1·718 (6) Å, and the Si···Si distance 3·209 (3) Å.

Introduction. The compound was prepared by reaction of Ph_3SiN_3 with Ph_3SiH (Tsai, Lehn & Marshall, 1970); crystals were grown from light petroleum. The space group was uniquely assigned from the systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. The intensities of 4486 unique reflections having $2° \leq \theta \leq 30°$ in the octant $+h$, $+k$, $+l$ (l = 0–14; $0° \leq \theta \leq 26{\cdot}247°$) were measured using a Stoe Stadi-2 diffractometer in the ω–2θ scan mode with a scan speed of 0·0167° s^{-1} in ω: backgrounds were measured at each end of the peak scan for a time of (scan time)/2. Standard reflections, measured after every 50 reflections, showed only small random deviations from their means. Lorentz and polarization but no absorption corrections were applied.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1976) and refined by full-matrix least squares with complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) for 2225 unique reflections having $F_o \geq 6\sigma(F_o)$. Anisotropic temperature factors were applied to Si, N and C; a common isotropic temperature factor was applied to the phenyl H atoms, which were placed in calculated positions, and a second isotropic parameter to the unique hydrogen. The position of the unique H atom was not well defined, and in the final cycles the N—H distance was fixed at 1·000 Å. With unit weights the refinement converged to $R = \sum\Delta/\sum F_o$ = 0·0774 and $R_G = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0·0795; using weights $w = 1/\sigma^2(F)$ the geometry of the phenyl rings was rather less satisfactory and all results quoted are for unit weights. Refinement of the alternative enantiomorph yielded identical R indices.†

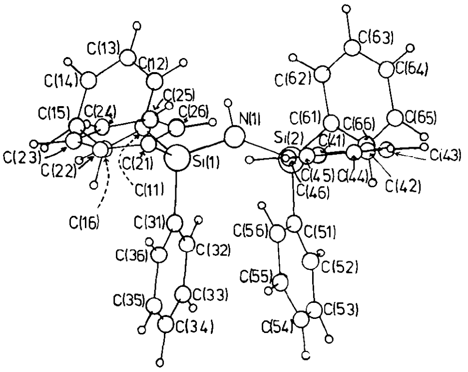

Fig. 1. The $(Ph_3Si)_2NH$ molecule showing the numbering of the atoms.

The final coordinates are listed in Table 1 and the geometry of the central $C_3SiNSiC_3$ fragment is given in Table 2. Fig. 1 shows the molecule and the numbering of the atoms. Least-squares planes are given in Table 3.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35823 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates* ($\times 10^4$), *and equivalent isotropic temperature parameters* (Å^2 $\times 10^3$)

	x	*y*	*z*	*U**
Si(1)	9044 (1)	3556 (1)	7445 (2)	33
Si(2)	9584 (1)	3448 (2)	10127 (2)	33
N	9469 (4)	3119 (5)	8660 (7)	43
C(11)	8553 (4)	2500 (6)	6776 (8)	35
C(12)	8749 (5)	1493 (7)	6905 (10)	51
C(13)	8379 (5)	722 (7)	6406 (14)	62
C(14)	7804 (5)	927 (8)	5760 (10)	60
C(15)	7590 (5)	1904 (7)	5631 (10)	59
C(16)	7961 (4)	2667 (6)	6155 (9)	45
C(21)	9654 (4)	4039 (6)	6309 (9)	39
C(22)	10321 (5)	4180 (9)	6617 (11)	67
C(23)	10753 (7)	4616 (13)	5720 (15)	83
C(24)	10527 (9)	4820 (11)	4624 (18)	87
C(25)	9858 (7)	4660 (9)	4257 (13)	86
C(26)	9442 (5)	4271 (8)	5183 (10)	62
C(31)	8451 (4)	4581 (6)	7836 (8)	39
C(32)	7891 (4)	4393 (7)	8506 (11)	53
C(33)	7434 (6)	5164 (9)	8767 (14)	75
C(34)	7523 (5)	6101 (8)	8328 (11)	53
C(35)	8073 (6)	6301 (7)	7694 (13)	61
C(36)	8546 (5)	5554 (7)	7434 (13)	61
C(41)	9054 (4)	2610 (5)	11110 (8)	34
C(42)	8465 (4)	2233 (6)	10679 (10)	48
C(43)	8050 (5)	1638 (7)	11402 (12)	60
C(44)	8229 (5)	1423 (7)	12526 (12)	53
C(45)	8826 (6)	1786 (7)	13007 (11)	63
C(46)	9242 (4)	2375 (7)	12274 (9)	52
C(51)	9380 (4)	4795 (6)	10421 (9)	41
C(52)	8990 (5)	5091 (7)	11186 (10)	57
C(53)	8774 (6)	6098 (9)	11446 (14)	75
C(54)	9140 (6)	6826 (8)	10907 (12)	66
C(55)	9616 (6)	6551 (7)	10047 (13)	60
C(56)	9742 (5)	5518 (6)	9786 (10)	56
C(61)	10484 (4)	3268 (6)	10540 (8)	39
C(62)	10842 (4)	2492 (7)	10043 (11)	56
C(63)	11512 (5)	2363 (9)	10379 (12)	59
C(64)	11815 (4)	2988 (8)	11179 (10)	55
C(65)	11458 (5)	3761 (7)	11638 (11)	56
C(66)	10796 (4)	3898 (7)	11314 (9)	46

* Equivalent isotropic temperature parameters are defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij}.

Table 2. *Geometry of the* $C_3SiNSiC_3$ *fragment*

(*a*) Distances (Å)

Si(1)—N	1·718 (8)	Si(2)—N	1·722 (8)
Si(1)—C(11)	1·874 (8)	Si(2)—C(41)	1·896 (8)
Si(1)—C(21)	1·883 (9)	Si(2)—C(51)	1·870 (9)
Si(1)—C(31)	1·864 (8)	Si(2)—C(61)	1·881 (8)
	Si(1)···Si(2)	3·209 (3)	

(*b*) Angles (°)

N—Si(1)—C(11)	109·1 (4)	N—Si(2)—C(41)	109·5 (4)
N—Si(1)—C(21)	109·5 (4)	N—Si(2)—C(51)	112·6 (4)
N—Si(1)—C(31)	112·2 (4)	N—Si(2)—C(61)	109·4 (4)
C(11)—Si(1)—C(21)	109·0 (4)	C(41)—Si(2)—C(51)	109·8 (4)
C(21)—Si(1)—C(31)	109·0 (4)	C(51)—Si(2)—C(61)	106·8 (3)
C(31)—Si(1)—C(11)	108·0 (4)	C(61)—Si(2)—C(41)	108·7 (4)
	Si(1)—N—Si(2)	138·1 (4)	

Table 3. *Least-squares planes*

Planes are defined in orthogonal ångström coordinates by the equation: $Ax + By + Cz + D = 0$.

Plane		*A*	*B*	*C*	*D*
1	C(11)—C(16)	0·534 (4)	0·079 (7)	−0·842 (2)	7·720 (14)
2	C(21)—C(26)	0·228 (3)	−0·926 (3)	−0·300 (3)	7·265 (18)
3	C(31)—C(36)	−0·502 (4)	−0·230 (2)	−0·833 (2)	7·197 (17)
4	C(41)—C(46)	0·472 (4)	−0·821 (2)	−0·320 (1)	7·746 (7)
5	C(51)—C(56)	−0·685 (28)	0·028 (4)	−0·728 (3)	7·469 (31)
6	C(61)—C(66)	0·286 (8)	0·591 (3)	−0·755 (1)	6·087 (10)

Angles between planes (°)

Plane	2	3	4	5	6
1	72·4 (12)	65·5 (3)	62·8 (4)	75·6 (9)	33·4 (6)
2		69·6 (11)	15·3 (6)	87·9 (14)	−75·2 (6)
3			77·3 (2)	19·2 (25)	69·6 (3)
4				−83·5 (8)	−83·8 (3)
5					68·3 (6)

Discussion. The structure comprises isolated molecules (Fig. 1): there are no short N···N distances or intermolecular Si···N distances indicative of molecular association. The Si—N—Si angle, 138·1 (4)°, is the largest so far observed in a compound of type $(R_3Si)_2NH$ and the mean Si—N distance, 1·718 (6) Å, is the shortest (Table 4).

In both $(R_3Si)_2O$ and $(R_3Si)_2NH$ compounds (R = H,Me,Ph) the species having R = Ph exhibit Si···Si distances substantially longer than the 3·10 Å expected as the limiting contact distance, which is reasonably close to the values found in both series for R = H or Me (Table 4). However, neither the large SiXSi angles nor the Si···Si distances found when R = Ph can plausibly be ascribed to repulsive interactions between phenyl groups; as in $[(PhCH_2)_3Si]_2O$ where the phenyl groups on different Si atoms are very well separated, the Si—O—Si angle is again 180° (Glidewell & Liles, 1981).

The Si—C distances span the range 1·864 (8) to 1·896 (8) Å with a mean of 1·878 (10) Å, typical of those found in other phenyl–silicon compounds (Glidewell & Liles, 1978). The internal angles at the C(i1) (i = 1–6) atoms in the phenyl rings have a mean

Table 4. *Geometry of some* $R_3SiXSiR_3$ (X = O, NH) *molecules*

	Si—*X* (Å)	Si···Si (Å)	Si—*X*—Si (°)	Reference
$H_3SiNHSiH_3$	1·725 (3)	3·097 (6)	127·7 (1)	(*a*)
$Me_3SiNHSiMe_3$	1·735 (12)	3·085 (49)	125·5 (18)	(*b*)
$Ph_3SiNHSiPh_3$	1·718 (6)	3·209 (3)	138·1 (4)	This work
$H_3SiOSiH_3$	1·631 (6)	3·086 (2)	142·2 (3)	(*c*)
$Me_3SiOSiMe_3$	1·626 (5)	3·132 (1)	148·8 (2)	(*c*)
$Ph_3SiOSiPh_3$	1·616 (1)	3·232 (1)	180·0 (0)	(*d*)

References: (*a*) Rankin *et al.* (1969). (*b*) Robiette *et al.* (1968). (*c*) Barrow, Ebsworth & Harding (1979). (*d*) Glidewell & Liles (1978).

value of 118·5 (11)°, typical of phenyl rings bound to silicon (Domenicano, Vaciago & Coulson, 1975). The C—C distances range from 1·34 (3) to 1·45 (2) Å with a mean of 1·39 (2) Å.

The $(Ph_3Si)_2NH$ molecule has no internal symmetry in the crystal, as shown both by the Si—C distances (Table 2) and by the angles between the phenyl planes (Table 3).

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References

Barrow, M. J., Ebsworth, E. A. V. & Harding, M. M. (1979). *Acta Cryst.* B**35**, 2093–2099.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1896.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 1630–1641.

Glidewell, C. & Liles, D. C. (1978). *Acta Cryst.* B**34**, 124–128.

Glidewell, C. & Liles, D. C. (1981). Unpublished work.

Rankin, D. W. H., Robiette, A. G., Sheldrick, G. M., Sheldrick, W. S., Aylett, B. J., Ellis, I. A. & Monaghan, J. J. (1969). *J. Chem. Soc. A*, pp. 1224–1227.

Robiette, A. G., Sheldrick, G. M., Sheldrick, W. S., Beagley, B., Cruickshank, D. W. J., Monaghan, J. J., Aylett, B. J. & Ellis, I. A. (1968). *Chem. Commun.* pp. 909–910.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Tsai, T., Lehn, W. & Marshall, C. J. (1970). *J. Organomet. Chem.* **22**, 387–393.

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5-Benzylidene-2-(*p*-chlorobenzyl)cyclopentanone – a Photodimerizable Crystal

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Abstract. $C_{19}H_{17}ClO$, $M_r = 296{\cdot}8$, monoclinic, $P2_1/c$, $a = 17{\cdot}175$ (4), $b = 10{\cdot}587$ (3), $c = 8{\cdot}796$ (5) Å, $\beta = 76{\cdot}33$ (9)°, $Z = 4$, $D_x = 1{\cdot}269$ Mg m^{-3}. Final $R = 0{\cdot}055$ for 1728 independent reflections. Molecules form incipient dimers across centres of symmetry such that the intermolecular separation of reactive double bonds is 4·027 (5) Å.

Introduction. In a study of the growth of crystallographically oriented product in the topochemical dimerization of 2-benzyl-5-benzylidenecyclopentanone (BBCP) derivatives (Nakanishi, Jones & Thomas, 1980), we have observed that solid-state photoreactivity may be controlled by varying both the nature and position of substitution within the molecule. Thus, whilst 2-benzyl-5-(*p*-methylbenzylidene)cyclopentanone and its chloro analogue (B*p*ClBCP) are photostable, 5-benzylidene-2-(*p*-methylbenzyl)cyclopentanone and its chloro analogue (*p*ClBBCP) are photoreactive (Jones, Nakanishi, Theocharis & Thomas, 1980). The present study was undertaken as part of an investigation of the effect on crystal packing of varying the nature and position of substitution.

*p*ClBBCP was prepared by a method similar to that described by Forward & Whiting (1969). Single crystals were grown by evaporation of a methanol–chloroform solution. The specimen used for structure analysis was a fragment of a plate, 0·15 × 0·20 × 0·20 mm. The lattice constants and intensities were obtained from measurements on a Philips four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Reflections within the range $2\theta < 150°$ were collected in a 2θ–ω scan mode at a scanning rate of 4° min^{-1}. 1728 independent reflections had $|F_o| > 5\sigma(F_o)$ and were used for the determination. No correction was made for absorption.

The structure was determined by direct methods and refined by block-diagonal least squares. Isotropic H atoms were first located geometrically and then refined. Full-matrix refinement was carried out at the final stage to give $R = 0{\cdot}055$.*

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