

Table 6. Selected torsional angles ($^{\circ}$) for (I), (II) and (III)

E.s.d.'s are $\sim 0.3^{\circ}$.

	(I)	(II)	(III)		(I)	(II)	(III)
N(4)—C(8)—C(1)—C(9)	162.5	168.4	165.8	C(2)—O(3)—C(1)—C(2)	99.9	97.5	98.6
C(8)—C(1)—C(9)—O(2)	173.3	115.2	122.6	N(4)—C(8)—C(1)—C(2)	7.5	14.5	10.6
C(1)—C(2)—C(3)—N(4)	11.1	15.5	15.4	N(4)—C(8)—C(7)—C(6)	2.2	39.0	34.9
C(8)—C(1)—C(2)—C(3)	2.2	0.6	2.8	N(4)—C(8)—C(7)—O(1)	161.6	5.8	83.0
N(4)—C(8)—C(1)—O(3)	56.6	8.6	52.2	C(8)—C(7)—C(6)—C(5)	32.7	38.2	37.4
N(4)—C(3)—C(2)—O(3)	53.5	49.1	49.7	C(7)—C(6)—C(5)—N(4)	41.2	23.7	26.7
C(1)—O(3)—C(2)—C(3)	99.1	99.3	99.5	C(7)—C(8)—N(4)—C(5)	13.5	25.0	19.2

Table 7. Intermolecular distances (\AA)

E.s.d.'s for N...O distances are $\sim 0.004 \text{\AA}$.

	(I)	(II)	(III)	van der Waals distance
N(4)...O(2)	2.70	2.73	2.77	2.90
N(4)...H(O2)	1.76	1.84	1.86	2.70

All three structures show intermolecular contacts between N(4) and O(2) (Table 7) which are somewhat shorter than the combined van der Waals radii. The N(4)...H(O2) distances confirm hydrogen bonding (Hamilton & Ibers, 1968). The orientation of the C(9) hydroxyl [O(2)] seems to be influenced by the position of the epoxide oxygen [O(3)], although the real distance O(2)...O(3) 2.887 (I), 2.802 (II) and 3.699 \AA (III) is greater than the O...O van der Waals distance. Finally, the ORTEP views of (I), (II) and (III) (Figs. 1, 2 and 3) indicate that the C(9)—OH and C(7)—OH bonds are *anti* to each other in each case.

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Structure of 1,8-Bis(trimethylsilyl)naphthalene, C₁₆H₂₄Si₂

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Abstract. $M_r = 272.5$, orthorhombic, $Pna2_1$, $a = 183$ (1) K, $R = 0.0499$ for 810 observed reflections. Exhibiting non-crystallographic twofold rotation symmetry, the molecular structure displays effects of intramolecular strain associated with bulky substituent

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References

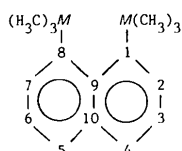
- CULVENOR, C. C. J. (1968). *J. Pharm. Sci.* **57**, 1112–1117.
 GELBAUM, L. T., GLINSKI, J. A., VANDERVEER, D. & ZALKOW, L. H. (1985). *Acta Cryst.* C**41**, 1342–1345.
 GELBAUM, L. T., GORDON, M. M., MILES, M. & ZALKOW, L. H. (1982). *J. Org. Chem.* **47**, 2501–2504.
 HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 16. New York: Benjamin.
 JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
 MCLEAN, E. K. (1970). *Pharmacol. Rev.* **22**, 479–483.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 ROITMAN, J. N. (1983). *Am. Chem. Soc. Symp. Ser.* **234**, 345–378.
 SHELDRIK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
 SMITH, L. W. & CULVENOR, C. C. J. (1981). *J. Nat. Prod.* **44**, 129–152.
 WARREN, F. L. (1970). *The Alkaloids*, Vol. XII, edited by R. H. F. Manske, ch. 4, pp. 246–262. London, New York: Academic Press.
 WARREN, F. L. & VON KLEMPERER, M. E. (1958). *J. Chem. Soc.* pp. 4574–4575.
 ZALKOW, L. H., BONETTI, S., GELBAUM, L., GORDON, M. M., PATEL, B. B., SHANI, A. & VANDERVEER, D. (1979). *J. Nat. Prod.* **42**, 603–614.
 ZALKOW, L. H., GLINSKI, J. A., GELBAUM, L. T., FLEISCHMANN, T. J., MCGOWAN, L. S. & GORDON, M. M. (1985). *J. Med. Chem.* In the press.

Table 1. *Experimental parameters for 1,8-bis(trimethylsilyl)naphthalene*

Crystal habit	Needle-like, colorless
Crystal dimensions	0.10 × 0.10 × 0.30 mm
Diffractometer	Enraf-Nonius CAD-4 with graphite monochromator
Reflections for lattice parameters	25
Scan mode	ω - θ
Scan rate	2 to 20° min ⁻¹ (in ω)
2 θ _{max}	60°
Range of <i>hkl</i>	43 11 8 to 0 0 1
Reflections measured	2767
Unique reflections	2560
Intensities > 3 $\sigma(I)$	810 (used for structure analysis)
Standard reflections	Three showing -1.7% relative change
Extinction parameter	< 1.0 × 10 ⁻⁷
Structure derivation	Direct methods and ($F_o - F_c$) maps
Least-squares refinement	Full-matrix using F
Hydrogen-atom introduction	Calculated based on structure type, positions refined on last LS cycle
E.s.d. of unit observation	1.19
Final <i>R</i> index	0.0499
Final weighted <i>R</i> index	0.0540
Weighting scheme	$w = 4F^2/\sigma^2(F^2)$
(Δ/σ) _{max}	0.26 (scale factor)
	0.17 (atom positional parameters)
Max. height in final difference	±0.3 e Å ⁻³
Fourier synthesis	<i>SDP</i> (Frenz, 1982)
Data processing	Modified for TEXRAY 230 system, Molecular Structure Corporation

groups at peri positions of the naphthalene ring [a 15.3° twist relative to the C(9)–C(10) bond and deflection of Si from the mean molecular plane].

Introduction. Steric interactions associated with peri-substituted naphthalenes are so great that the naphthalene skeleton is severely distorted from planar geometry (Handel, White, Franck, Yuh & Allinger, 1977). Previous studies suggested that molecular deformations in 1,8-bis(trimethylelement)naphthalenes should follow the order 1(*a*) >> 1(*b*) > (*c*) > 1(*d*) (Blount, Cozzi, Damewood, Iroff, Sjostrand & Mislow, 1980). Completion of the comparisons now becomes possible following the recent synthesis of the silicon analog (Sooriyakumaran & Boudjouk, 1982).



- 1(*a*), *M* = C
 1(*b*), *M* = Si
 1(*c*), *M* = Ge
 1(*d*), *M* = Sn

Experimental. A sample of 1,8-bis(trimethylsilyl)naphthalene was submitted to the Molecular Structure Corporation for collection of X-ray diffraction intensity data. Experimental parameters are listed in Table 1. No absorption correction applied. All non-hydrogen atoms refined anisotropically. Only on the final least-squares cycle were hydrogen positions allowed to refine to establish e.s.d.'s. The scale factor and extinction

coefficient were also refined. Atomic scattering factors and dispersion-correction parameters are those tabled in the *SDP*: atomic scattering factors derived from Cromer & Waber (1974), dispersion corrections from Ibers & Hamilton (1964) and Cromer (1974).

Discussion. The molecular structure and non-hydrogen-atom identification is found in Fig. 1. Fractional atomic coordinates are presented in Table 2.* Important conformational and geometric parameters are presented in Table 3.

1,8-Bis(trimethylsilyl)naphthalene displays the effect of intramolecular strain associated with bulky substituent groups at the peri positions. The 15.3° twist of the C(1)–C(9)–C(8) and C(4)–C(10)–C(5) planes about the C(9)–C(10) axis, the near 2 symmetry of the molecule, and the 0.97 Å deflection of the peri (CH₃)₃Si– groups from the mean molecular plane confirm the resemblance to other members of the homologous series of 1,8-bis(trimethylelement)naphthalenes. Closer examination of the bonding parameters collected in Table 4 shows 1(*b*) to be more like 1(*c*) than 1(*a*). The alignment of 1(*b*) in relation to the orthorhombic crystallographic axes is shown in Fig. 2.

The unit-cell volumes of 1(*b*), 1(*c*) and 1(*d*) decrease with each successive decrease in size of *M*.

	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>V</i>
1(<i>b</i>)	30.849 (1) Å	8.248 (2) Å	6.381 (2) Å	90.00°	1623 Å ³
1(<i>c</i>)	13.045 (2)	10.157 (1)	12.701 (2)	91.12 (1)	1683
1(<i>d</i>)	13.393 (2)	10.185 (1)	12.976 (2)	92.99 (1)	1768

* Lists of anisotropic displacement parameters, hydrogen-atom coordinates, observed and calculated structure factors, and a complete table of interatomic bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42258 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

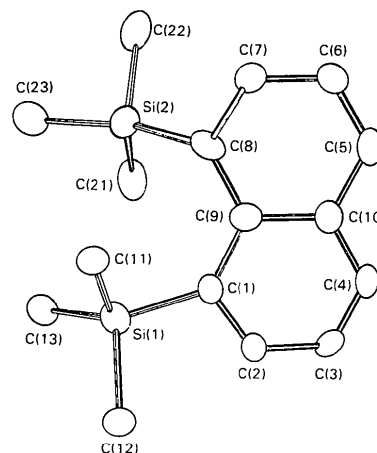


Fig. 1. Molecular structure of 1,8-bis(trimethylsilyl)naphthalene showing atom identification scheme. Hydrogen atoms are not included, for clarity in presentation.

Financial support by the National Science Foundation through Grant CHE-8311371 for assistance in acquisition of the TEXRAY 230 system and by the Air Force Office of Scientific Research through Grant 84-0008 is gratefully acknowledged.

Table 2. Positional and equivalent isotropic displacement parameters for 1,8-bis(trimethylsilyl)naphthalene

Atom numbering as in Fig. 1. Numbers in parentheses indicate e.s.d.'s. Anisotropically refined atom displacement parameters are given in the form of the equivalent isotropic displacement parameters defined as: $\frac{1}{3}(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3))$.

	x	y	z	$B_{eq}(\text{\AA}^2)$
Si(1)	0.12037 (8)	0.1659 (3)	0.1110	1.89 (4)
Si(2)	0.17885 (8)	-0.2174 (3)	0.2834 (6)	1.77 (4)
C(1)	0.0892 (3)	-0.027 (1)	0.051 (1)	1.6 (2)
C(2)	0.0578 (3)	-0.010 (1)	-0.105 (2)	2.0 (2)
C(3)	0.0217 (3)	-0.112 (1)	-0.126 (2)	2.0 (2)
C(4)	0.0148 (3)	-0.224 (1)	0.025 (2)	2.2 (2)
C(5)	0.0348 (3)	-0.356 (1)	0.359 (2)	2.1 (2)
C(6)	0.0635 (3)	-0.387 (1)	0.506 (2)	2.2 (2)
C(7)	0.1056 (3)	-0.321 (1)	0.493 (2)	2.2 (2)
C(8)	0.1184 (3)	-0.219 (1)	0.333 (1)	1.6 (2)
C(9)	0.0850 (3)	-0.163 (1)	0.189 (1)	1.4 (2)
C(10)	0.0445 (3)	-0.250 (1)	0.189 (1)	1.9 (2)
C(11)	0.1196 (3)	0.190 (1)	0.402 (2)	2.1 (2)
C(12)	0.0890 (3)	0.341 (1)	0.002 (2)	2.8 (2)
C(13)	0.1756 (3)	0.187 (1)	-0.013 (2)	2.5 (2)
C(21)	0.2120 (3)	-0.054 (1)	0.411 (2)	2.7 (2)
C(22)	0.1868 (3)	-0.237 (1)	-0.001 (2)	2.9 (2)
C(23)	0.2014 (3)	-0.406 (1)	0.389 (2)	2.6 (2)

Table 3. Geometric parameters of 1,8-bis(trimethylsilyl)naphthalene

Numbers in parentheses indicate e.s.d. of the last digit. Atom numbering as in Fig. 1.

Interatomic distances (Å)			
Si(1)—C(1)	1.894 (10)	Si(2)—C(8)	1.895 (10)
Si(1)—C(11)	1.869 (13)	Si(2)—C(21)	1.89 (2)
Si(1)—C(12)	1.868 (13)	Si(2)—C(22)	1.84 (2)
Si(1)—C(13)	1.892 (12)	Si(2)—C(23)	1.838 (13)
C(1)—C(9)	1.438 (12)	C(8)—C(9)	1.455 (13)
C(2)—C(3)	1.409 (14)	C(6)—C(7)	1.416 (14)
C(4)—C(10)	1.406 (14)	C(5)—C(10)	1.428 (14)
C(1)—C(2)	1.392 (14)	C(7)—C(8)	1.380 (14)
C(9)—C(10)	1.436 (12)		

Bond angles (°)			
C(1)—Si(1)—C(13)	116.7 (5)	C(8)—Si(2)—C(21)	118.1 (5)
C(1)—Si(1)—C(11)	106.3 (5)	C(8)—Si(2)—C(22)	107.0 (6)
C(1)—Si(1)—C(12)	107.9 (5)	C(8)—Si(2)—C(23)	107.8 (5)
C(11)—Si(1)—C(13)	114.7 (6)	C(21)—Si(2)—C(22)	114.7 (7)
C(11)—Si(1)—C(12)	106.3 (6)	C(22)—Si(2)—C(23)	104.1 (7)
C(12)—Si(1)—C(13)	104.1 (6)	C(21)—Si(2)—C(23)	104.0 (6)
Si(1)—C(1)—C(9)	125.7 (7)	Si(2)—C(8)—C(9)	126.0 (7)
Si(1)—C(1)—C(2)	114.1 (7)	Si(2)—C(8)—C(7)	114.2 (8)
C(2)—C(1)—C(9)	117.0 (9)	C(7)—C(8)—C(9)	117.5 (9)
C(1)—C(2)—C(3)	123. (1)	C(6)—C(7)—C(8)	123. (1)
C(2)—C(3)—C(4)	118. (1)	C(5)—C(6)—C(7)	120. (1)
C(3)—C(4)—C(10)	122. (1)	C(6)—C(5)—C(10)	122. (1)
C(1)—C(9)—C(10)	118.0 (9)	C(8)—C(9)—C(10)	117.2 (9)
C(4)—C(10)—C(9)	120. (1)	C(5)—C(10)—C(9)	119.0 (9)
C(1)—C(9)—C(8)	124.9 (8)	C(4)—C(10)—C(5)	121.3 (9)

Table 4. Selected structural parameters for 1,8-bis[(H₃C)₃M]naphthalene

Chemically equivalent values are reported as averages. Atom numbering as in Fig. 1.

	M=C†	M=Si	M=Ge†	M=Sn†
Bond distances (Å)				
M—C _{methyl} *	1.539	1.866	1.950	2.140
M—C(1/8)	1.558	1.894	1.974	2.162
Bond angles (°)				
M—C(1/8)—C(9)	125.7	125.8	125.2	125.5
C(1/8)—C(9)—C(10)	115.1	117.6	117.0	117.2
Torsion angles (°)				
M(1)—C(1)—C(8)—M(2)	-68.6	-57.3	-54.3	-51.3
C(9)—C(1/8)—M(1/2)—C(11/22)	8.5	-28.3	-30.3	-30.7
C(1/8)—C(9)—C(10)—C(4/5)	19.3	14.9	11.3	8.9

* Average of the six M—C_{methyl} bond distances.

† Values derived from Blount *et al.* (1980).

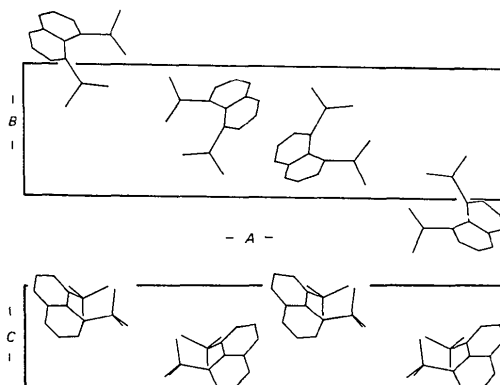


Fig. 2. [001] and [010] projections of the crystal structure of 1,8-bis(trimethylsilyl)naphthalene.

References

- BLOUNT, J. F., COZZI, F., DAMEWOOD, J. R. JR, IROFF, L. D., SJOSTRAND, U. & MISLOW, K. (1980). *J. Am. Chem. Soc.* **102**, 99–103.
- CROMER, D. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- FRENZ, B. A. (1982). *Structure Determination Package*. Enraf-Nonius, Delft.
- HANDEL, J., WHITE, J. G., FRANCK, R. W., YUH, U. H. & ALLINGER, N. L. (1977). *J. Am. Chem. Soc.* **99**, 3345–3349.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- SOORIYAKUMARAN, R. & BOUDJOUK, P. (1982). *Organometallics*, **1**, 218–219.