

## References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Pillai, M. R. A., Barnes, C. L., John, C. S., Troutner D. E. & Schlemper, E. O. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 949–953.
- Pillai, M. R. A., Barnes, C. L. & Schlemper, E. O. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 719–723.
- Pillai, M. R. A., Barnes, C. L. & Schlemper, E. O. (1994). *Polyhedron*, **13**, 701–708.
- Pillai, M. R. A., John, C. S., Lo, J. M., Schlemper, E. O. & Troutner, D. E. (1990). *Inorg. Chem.* **29**, 1850–1856.
- Pillai, M. R. A. & Schlemper, E. O. (1994). *J. Chem. Cryst.* **24**, 129–132.

*Acta Cryst.* (1997). **C53**, 1329–1331

## 1,2,4,5-Tetrakis(trimethylsilylmethyl)-benzene at 150 K

NORBERT NAGEL, MANSSUR ANSARI AND HANS BOCK

*Institut für Anorganische Chemie, der Universität Frankfurt, Marie-Curie-Str. 11, 60439 Frankfurt/Main, Germany.  
E-mail: nagel@bock.anorg.chemie.uni-frankfurt.de*

(Received 10 February 1997; accepted 4 April 1997)

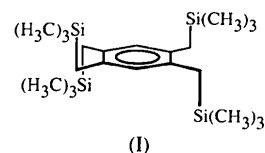
## Abstract

The title compound,  $C_{22}H_{46}Si_4$ , crystallizes in space group *Fddd* with crystallographic symmetry 222. Steric overcrowding by the bulky ligands is avoided by arranging the trimethylsilyl groups alternately above and below the benzene plane in skeletal  $D_2$  symmetry.

## Comment

Molecular state properties of organosilicon compounds are strongly influenced by substituent effects (Bock, 1989). It is well documented in the literature that  $\pi$ -hydrocarbons substituted by trimethylsilyl groups,  $-Si(CH_3)_3$ , e.g. 1,2,4,5-tetrakis(trimethylsilyl)benzene (Bock, Ansari, Nagel & Havlas, 1995; Sekiguchi, Ebata, Kabuto & Sakurai, 1991a), hexakis(trimethylsilyl)benzene (Sakurai, Ebata, Kabuto & Sekiguchi, 1990; Sekiguchi, Ebata, Kabuto & Sakurai, 1991b; Podlogar, Glauser, Rodriguez & Raber, 1988) 9,10-bis(trimethylsilyl)anthracene (Bock, Ansari, Nagel & Claridge, 1995) or 9,10-bis(diisopropylsilyl)anthracene (Bock, Ansari, Nagel & Claridge, 1996), easily form

radical anions on one-electron reduction at lithium or sodium metal mirrors. In contrast, substitution by trimethylsilylmethyl groups,  $-CH_2Si(CH_3)_3$ , facilitates the one-electron oxidation to radical cations (Bock & Kaim, 1978; Bock, Meuret & Ruppert, 1993). The rather low first ionization energy of 1,2,4,5-tetrakis(trimethylsilylmethyl)benzene ( $IE_1^V = 7.10$  eV) allows its oxidation with  $AlCl_3$  in  $CH_2Cl_2$  and the radical cation generated has been characterized by its ESR spectrum (Bock & Kaim, 1978). So far, however, no suitable single crystals of the oxidation product have been grown and, therefore, only the crystal structure of the neutral compound (I) is presented.



1,2,4,5-Tetrakis(trimethylsilylmethyl)benzene, (I), crystallizes in space group *Fddd* (No. 70) with a quarter of a molecule inside the asymmetric unit. The molecule is located around the intersection of three crystallographic twofold axes (Fig. 1) [Wyckoff position 222 (*a*); origin at  $-1$  at *ddd*, at  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$  from 222 (choice 2); Hahn, 1983]. The four trimethylsilylmethyl groups are oriented alternately above and below the six-membered ring plane with  $\omega(C1-C2-C10-Si1) = 82.40(14)^\circ$  and the methylene centres are twisted out of plane by  $\pm 0.07(2)$  Å, each towards the attached trimethylsilyl group. The conformational arrangement with alternating trimethylsilyl groups around the ring corresponds to that of hexakis(trimethylsilylmethyl)benzene, which in the crystal adopts  $S_3$  symmetry and is located around a centre of inversion on a threefold axis (Bock, Meuret & Ruppert, 1993). Bond lengths and angles of both compounds are very similar and within the usual range of organosilicon compounds (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). In the crystal structure, all phenyl rings are oriented paral-

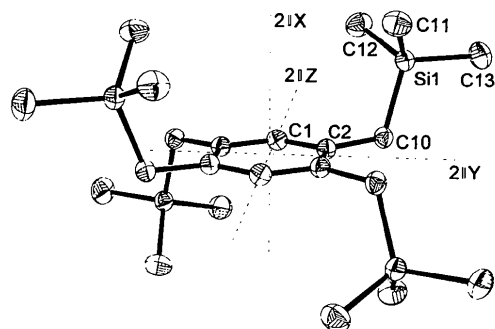


Fig. 1. A view of the title compound with anisotropic displacement ellipsoids for C and Si atoms at the 50% probability level, crystallographic symmetry elements intersecting the molecule and our numbering scheme of the asymmetric unit.

lel to the *yz* plane (Fig. 2), but the bulky trimethylsilylmethyl substituents prevent the  $\pi$ - $\pi$  interactions (Nishio, Umezawa, Hirota & Takeuchi, 1995; Hunter, 1994; Hobza, Selzle & Schlag, 1994) commonly found in crystal structures of  $\pi$ -hydrocarbons with sterically less demanding substituents (*cf.* Nagel, Eller & Bock, 1996). The shortest intermolecular C...C distance of 3.936 (3) Å between C11 and C11(- $\frac{1}{4}$  - *x*,  $\frac{7}{4}$  - *y*, *z*) suggests only weak van der Waals interactions between the molecules.

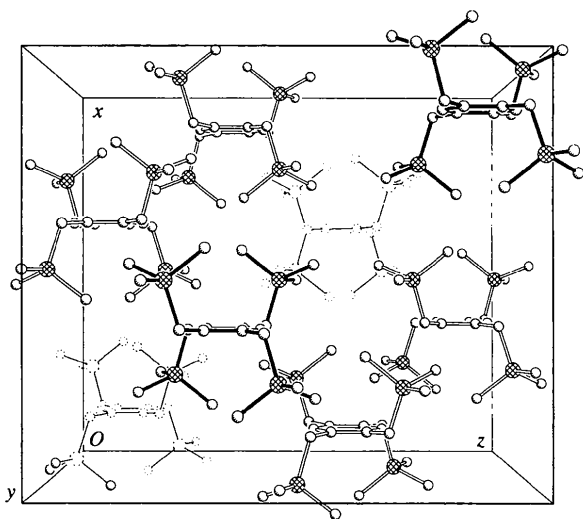


Fig. 2. Unit cell viewed along the *y* axis.

## Experimental

The solvents THF and *n*-hexane were refluxed for several days over a Na-K alloy. Carbon tetrachloride and chloroform were twice refluxed for 8 h over P<sub>4</sub>O<sub>10</sub> and then kept under dry argon. The literature procedure (Bock & Kaim, 1978) has been modified as follows: for the preparation of 1,2,4,5-tetrakis(bromomethyl)benzene, 1,2,4,5-tetramethylbenzene (15 g, 112 mmol), *N*-bromosuccinimide (80 g, 48 mmol) and 6 g of benzoyl peroxide were added to 300 ml of carbon tetrachloride and the mixture was carefully heated under reflux until the red-brown colour vanished. The hot mixture was filtered, the residue washed with hot carbon tetrachloride and the solution concentrated to about 100 ml. After cooling at 278 K for several hours, white crystals separated, which were recrystallized from chloroform to yield 5.86 g (12%) of 1,2,4,5-tetrakis(bromomethyl)benzene (m.p. 431 K; literature 433 K). Elemental analysis: calculated C 26.7, H 2.24%; experimental C 27.22, H 2.33%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS): 4.6 (*s*, 8H), 7.38 (*s*, 2H) p.p.m. For the preparation of 1,2,4,5-tetrakis(trimethylsilylmethyl)benzene, 1,2,4,5-tetrakis(bromomethyl)benzene (4 g, 8.9 mmol) was added to a stirred suspension of chlorotrimethylsilane (4.63 g, 42.6 mmol) and potassium (1.7 g, 42.6 mmol) in 150 ml of tetrahydrofuran and the mixture heated under reflux for 10 h. After filtering off the solid residues, the solution was hydrolyzed with 100 ml of water and extracted twice with 50 ml of diethyl ether. The combined extracts were dried over MgSO<sub>4</sub>, evaporated and the

residue was subjected to chromatography on silica (20 g) using *n*-hexane as the eluent. Evaporation of the solvent yielded 1.05 g (28%) of 1,2,4,5-tetrakis(trimethylsilylmethyl)benzene (m.p. 401–402 K; literature 402 K). Elemental analysis: calculated C 62.5, H 11.00%; experimental C 61.68, H 10.86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS): 0.01 (*m*, 36H), 1.88 (*s*, 8H), 6.5 (*s*, 2H) p.p.m. 1,2,4,5-Tetrakis(trimethylsilylmethyl)benzene (500 mg) was dissolved in 5 ml of chloroform and 5 ml of ethanol was added as a layer. After 2 d, colourless crystals suitable for X-ray structure determination had grown.

## Crystal data

C<sub>22</sub>H<sub>46</sub>Si<sub>4</sub>  
*M<sub>r</sub>* = 422.95  
 Orthorhombic  
*Fddd*  
*a* = 16.2226 (13) Å  
*b* = 17.8756 (15) Å  
*c* = 19.0452 (18) Å  
*V* = 5522.9 (8) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.017 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 96 reflections  
 $\theta$  = 10–18°  
 $\mu$  = 0.220 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block  
 0.60 × 0.45 × 0.40 mm  
 Colourless

## Data collection

Siemens P4 four-circle diffractometer  
 $\omega$  scan  
 Absorption correction: none  
 1664 measured reflections  
 1572 independent reflections  
 1298 reflections with *I* > 2 $\sigma$ (*I*)

*R*<sub>int</sub> = 0.025  
 $\theta_{\max}$  = 27.5°  
*h* = 0 → 21  
*k* = 0 → 23  
*l* = -1 → 24  
 3 standard reflections every 100 reflections  
 intensity decay: negligible

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.093  
*S* = 1.089  
 1572 reflections  
 68 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 7.9743P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.262$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.201$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

|     | <i>x</i>      | <i>y</i>     | <i>z</i>     | <i>U</i> <sub>eq</sub> |
|-----|---------------|--------------|--------------|------------------------|
| Si1 | 0.01246 (3)   | 0.79043 (2)  | 0.51812 (2)  | 0.02389 (14)           |
| C1  | 1/8           | 5/8          | 0.55369 (11) | 0.0231 (4)             |
| C2  | 0.12493 (9)   | 0.69390 (7)  | 0.58800 (7)  | 0.0219 (3)             |
| C10 | 0.12071 (10)  | 0.76484 (8)  | 0.54522 (8)  | 0.0245 (3)             |
| C11 | -0.05838 (11) | 0.78298 (10) | 0.59470 (9)  | 0.0368 (4)             |
| C12 | -0.02428 (11) | 0.72535 (10) | 0.44835 (10) | 0.0387 (4)             |
| C13 | 0.01272 (12)  | 0.88791 (10) | 0.48283 (10) | 0.0415 (4)             |

Table 2. Selected geometric parameters (Å, °)

|         |           |         |           |
|---------|-----------|---------|-----------|
| Si1—C11 | 1.862 (2) | C1—C2   | 1.394 (2) |
| Si1—C12 | 1.864 (2) | C1—C2'  | 1.394 (2) |
| Si1—C13 | 1.868 (2) | C2—C2'' | 1.409 (3) |
| Si1—C10 | 1.887 (2) | C2—C10  | 1.509 (2) |

|                |            |                |             |
|----------------|------------|----------------|-------------|
| C11—Si1—C12    | 108.45 (9) | C2—C1—C2'      | 124.1 (2)   |
| C11—Si1—C13    | 110.49 (9) | C1—C2—C2''     | 117.95 (9)  |
| C12—Si1—C13    | 109.06 (9) | C1—C2—C10      | 119.30 (13) |
| C11—Si1—C10    | 110.06 (7) | C2''—C2—C10    | 122.69 (8)  |
| C12—Si1—C10    | 109.96 (8) | C2—C10—Si1     | 113.19 (10) |
| C13—Si1—C10    | 108.82 (8) |                |             |
| C1—C2—C10—Si1  | 82.40 (14) | C12—Si1—C10—C2 | -72.52 (13) |
| C11—Si1—C10—C2 | 46.89 (13) | C13—Si1—C10—C2 | 168.09 (11) |

Symmetry codes: (i)  $\frac{1}{4} - x, \frac{3}{4} - y, z$ ; (ii)  $\frac{1}{4} - x, y, \frac{3}{4} - z$ .

Data were corrected for Lorentz and polarization effects. All C and Si centres were refined anisotropically, and all hydrogens were located from the difference map and placed in idealized positions using a riding model; C—H<sub>phenyl</sub> = 0.95, C—H<sub>methylene</sub> = 0.99 and C—H<sub>methyl</sub> = 0.98 Å. The torsion of the methyl hydrogens and the isotropic displacement parameters of all H centres were refined (methyl and methylene moieties were treated as rigid groups).

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC XP (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93 CIFTAB.

The project was supported by the A. Messer Foundation, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fonds der Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1201). Services for accessing these data are described at the back of the journal.

## References

- Bock, H. (1989). *Angew. Chem.* **101**, 1659–1682; *Angew. Chem. Int. Ed. Engl.* **28**, 1627–1650.
- Bock, H., Ansari, M., Nagel, N. & Claridge, R. F. C. (1995). *J. Organomet. Chem.* **501**, 53–60.
- Bock, H., Ansari, M., Nagel, N. & Claridge, R. F. C. (1996). *J. Organomet. Chem.* **521**, 51–63.
- Bock, H., Ansari, M., Nagel, N. & Havlas, Z. (1995). *J. Organomet. Chem.* **499**, 63–71.
- Bock, H. & Kaim, W. (1978). *Chem. Ber.* **111**, 3552–3572.
- Bock, H., Meuret, J. & Ruppert, K. (1993). *Chem. Ber.* **126**, 2237–2241.
- Hahn, Th. (1983). Editor. *International Tables for X-ray Crystallography*, Vol. A, 310–313. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Hobza, P., Selzle, H. L. & Schlag, E. W. (1994). *Chem. Rev.* **94**, 1767–1785.
- Hunter, C. A. (1994). *Chem. Soc. Rev.* pp. 101–109.
- Nagel, N., Eller, P. & Bock, H. (1996). *Acta Cryst.* **B52**, 562–568.
- Nishio, M., Umezawa, Y., Hirota, M. & Takeuchi, Y. (1995). *Tetrahedron*, **51**, 8665–8701.
- Orpen, A. G., Brammer, L., Allen, F. A., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, appendix A, pp. 751–784. Weinheim: VCH.
- Podlogar, B. L., Glauser, W. A., Rodriguez, W. R. & Raber, D. J. (1988). *J. Org. Chem.* **53**, 2127–2129.
- Sakurai, H., Ebata, K., Kabuto, C. & Sekiguchi, A. (1990). *J. Am. Chem. Soc.* **112**, 1799–1803.
- Sekiguchi, A., Ebata, K., Kabuto, C. & Sakurai, H. (1991a). *J. Am. Chem. Soc.* **113**, 7081–7082.
- Sekiguchi, A., Ebata, K., Kabuto, C. & Sakurai, H. (1991b). *J. Am. Chem. Soc.* **113**, 1464–1465.
- Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.

- Sheldrick, G. M. (1990b). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1997). **C53**, 1331–1334

## 3,5-Dinitro-2-[(R)-(-)-1-phenylethyl]-amino}pyridine

JACQUELINE M. COLE,† JUDITH A. K. HOWARD AND J. A. HUGH MACBRIDE

*Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England. E-mail: cole@ill.fr*

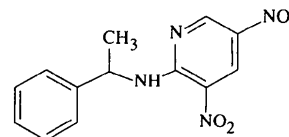
(Received 25 November 1996; accepted 9 April 1997)

## Abstract

The synthesis and crystal structure of the title compound, C<sub>13</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>, is reported. The compound displayed second harmonic generation and the results are reported. The molecular packing is described in conjunction with an investigation of the phase-matching ability of the compound.

## Comment

Developments in organic non-linear optical (NLO) materials over the past 20 years have triggered a prolific interest in this area of research. In particular, second harmonic generation (SHG) measurements of organic NLO compounds have already produced results which by far exceed those obtained from all known inorganic materials, e.g. LiNbO<sub>3</sub>. Moreover, the much broader scope in molecular design of organic materials compared to inorganics provides greater possibilities for improving the SHG response. For example, many pyridine derivatives have shown great promise in terms of SHG efficiency (Twieg, Azema, Jain & Cheng, 1982). The title complex, (I), was therefore studied for its NLO potential.



(I)

† Present address: Institut Laue Langevin, BP 156, 38042 Grenoble CEDEX 9, France.