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# Tetrakis(3,5-dimethoxyphenyl)silane

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**Key indicators**

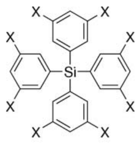
Single-crystal X-ray study
$T$ = 292 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.049
$wR$ factor = 0.149
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

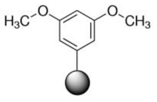
The title compound, $C_{32}H_{36}O_8Si$, crystallizes from $CH_2Cl_2$ by slow evaporation to produce a close-packed structure. In this structure, the molecules have crystallographic $\overline{4}$ symmetry and no guest molecules are included. In contrast, crystallization of the closely related tetrakis(3,5-dihydroxyphenyl)silane from a range of solvents is directed by phenolic hydrogen bonding to yield an open diamondoid network, which is filled by a combination of interpenetration and inclusion of guests.

## Comment

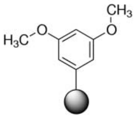
An effective strategy in crystal engineering relies on the use of molecules that associate predictably by forming multiple directional interactions. Such molecules, which have been called tectons from the Greek word for builder (Simard *et al.*, 1991), place their neighbors in predetermined positions and thereby provide the basic elements of a rational nanoscale construction set. In general, directional interactions and normal close packing cannot be optimized simultaneously, and tectonic assembly typically yields open molecular networks in which significant volume is filled by interpenetration of independent networks or by the inclusion of guests (Malek, Maris, Perron & Wuest, 2005; Malek, Maris, Simard & Wuest, 2005). For example, crystallization of tetrakis(3,5-dihydroxyphenyl)silane, (I), is directed by characteristic phenolic hydrogen bonding to give open diamondoid networks under various conditions (Saied *et al.*, 2005). The network produced by crystallization from methyl propiolate is fivefold interpenetrated, with no space remaining for the inclusion of guests, whereas crystallization from ethyl acetate, ethyl acrylate, tetrahydrofuran (THF) or dioxolane gives submaximally threefold interpenetrated structures in which approximately 50% of the volume is available for accommodating guests.



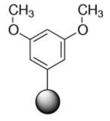
(I) (X = OH)
(II) (X = $OCH_3$)
(III) (X = H)



(IV)



(V)



(VI)

To place these observations in a broader context, to permit instructive comparisons and to test the notion that hydrogen bonding of OH groups in the resorcinol derivative, (I), plays a major role in directing crystallization, we grew crystals of the corresponding title octamethyl ether, (II), from $CH_2Cl_2$ and solved the structure (Figs. 1–5). As expected, the structure of (II) is close-packed, no guests are included, and cohesion arises primarily from van der Waals contacts. Each molecule

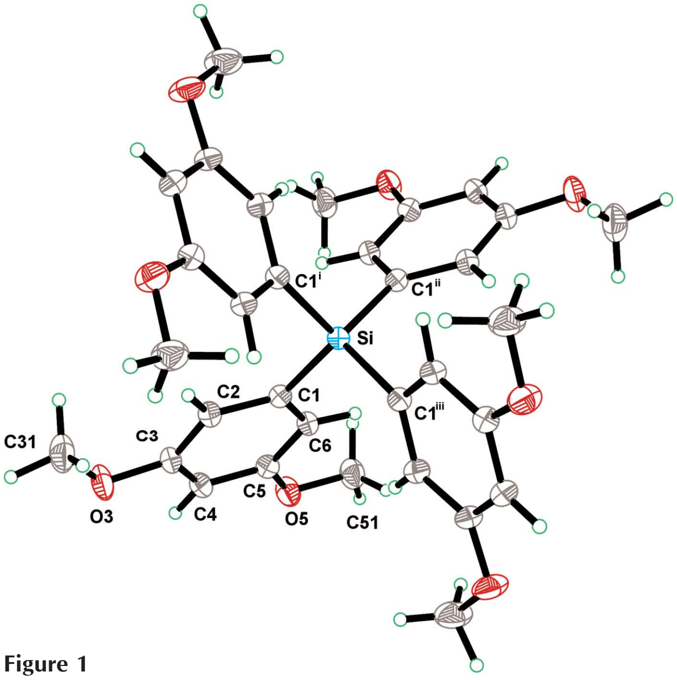


**Figure 1**
A view of the structure of the title compound when crystallized from $CH_2Cl_2$, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by spheres of arbitrary radii. [Symmetry codes: (i) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $-x, \frac{1}{2} - y, z$; (iii) $\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$.]

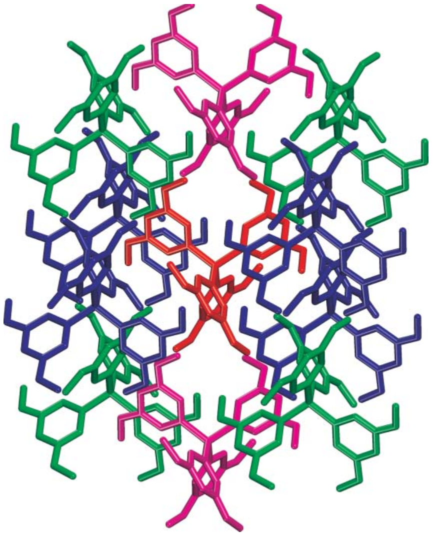


**Figure 2**
A view of a central molecule of (II) (red) with its ten neighbors (green, blue and purple). H atoms have been omitted to simplify the view. The four neighbors in green are separated from the central molecule by Si···Si distances of 11.330 (6) Å and engage only in van der Waals contacts. The four neighbors in blue are separated by Si···Si distances of 8.957 (6) Å and form both van der Waals contacts and weak C—H···O interactions, and the two neighbors in purple are separated along the *c* axis by Si···Si distances of 9.812 (4) Å and engage only in van der Waals contacts.

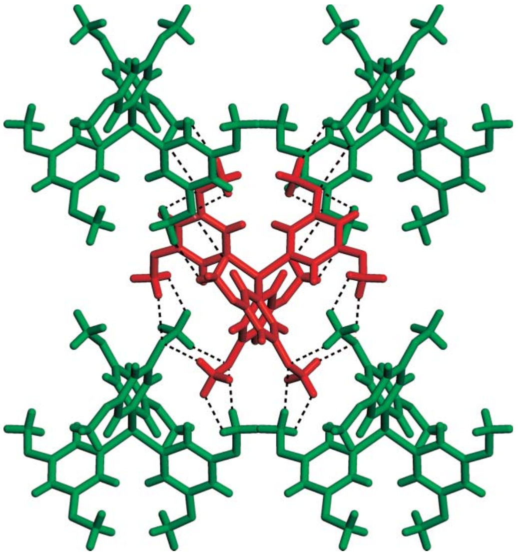


**Figure 3**
Detailed view of a central molecule of (II) (red) with the four neighbors (green) that are separated from the central molecule by Si···Si distances of 11.330 (6) Å. The shortest van der Waals contacts are represented by broken lines.

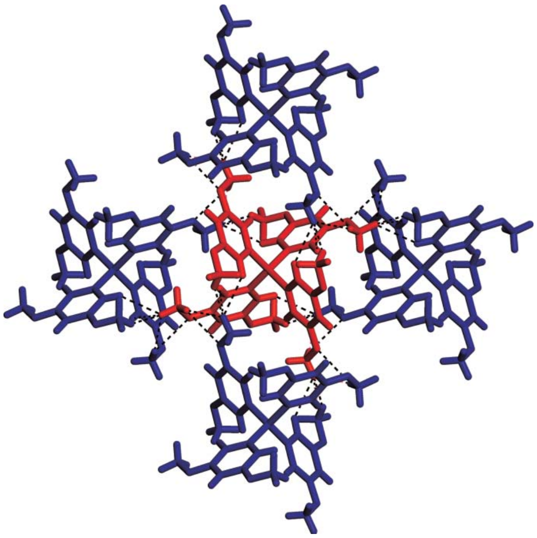


**Figure 4**
Detailed view of a central molecule of (II) (red) with the four neighbors (blue) that are separated from the central molecule by Si···Si distances of 8.957 (6) Å. The closest van der Waals contacts and the weak C—H···O interactions are represented by broken lines.

forms contacts with a total of ten neighbors (Fig. 2). Of these neighbors, four are separated from the central molecule by Si···Si distances of 11.330 (6) Å and engage only in van der Waals contacts (Fig. 3). Four others are separated by Si···Si distances of 8.957 (6) Å and form both van der Waals contacts and weak C—H···O interactions, with an H···O distance of 2.74 (2) Å (Fig. 4), and two more are separated along the *c* axis by Si···Si distances of 9.812 (4) Å and engage only in van der Waals contacts (Fig. 5). All other neighbors lie at Si···Si distances exceeding 13 Å and cannot be considered to interact with the central molecule. In each molecule of (II), the average C—Si—C angle of 109.47 (8)° is very close to the ideal tetrahedral value.

Tetraphenylsilane, (III), also crystallizes as a close-packed structure with no included guests (Glidewell & Sheldrick,

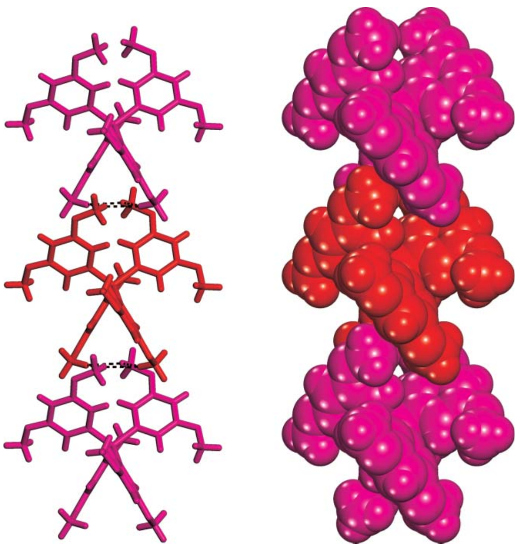


**Figure 5**
Detailed views of a central molecule of (II) (red) with the two neighbors (purple) that are separated along the *c* axis by Si···Si distances of 9.812 (4) Å. In both views, the *c* axis is vertical. In the left-hand view, the closest van der Waals contacts are shown as broken lines. In the right-hand view, the molecules are shown as CPK representations.

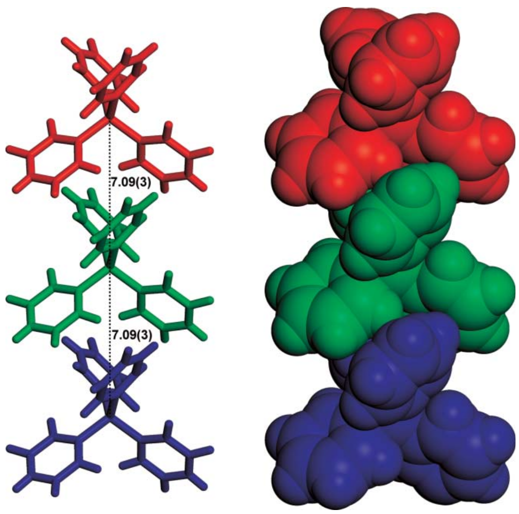


**Figure 6**
Detailed views of the phenyl embraces between a central molecule of tetraphenylsilane, (III), (green) with two neighbors (red and blue) that are separated along the *c* axis by Si···Si distances of 7.09 (3) Å (Glidewell & Sheldrick, 1971). In both views, the *c* axis is vertical. In the right-hand view, the molecules are shown as CPK representations.

1971). In that case, however, the absence of substituents allows a closer approach of the benzene rings, and cohesion is maintained by a combination of van der Waals interactions and edge-to-face aromatic interactions that define multiple phenyl embraces (Scudder & Dance, 2002). In the resulting structure, each molecule can be considered to interact with a total of 14 neighbors. Eight are separated from the central molecule by Si···Si distances of 8.845 (30) Å and engage only in van der Waals contacts. Four others are separated by Si···Si distances of 11.46 (3) Å and also form van der Waals contacts, and two more are separated along the *c* axis by Si···Si distances of 7.09 (3) Å and engage in phenyl embraces (Fig. 6). Again, the average C—Si—C angle [109.4 (4)°] is very close to the ideal tetrahedral value.

Molecules of tetraphenylsilane, (III), and tetrakis(3,5-dimethoxyphenyl)silane, (II), stack in a similar way along the *c* axis (Figs. 5 and 6), guided presumably by their shared molecular topology. However, the absence of substituents allows a much closer approach in the case of tetraphenylsilane [Si···Si 7.09 (3) Å] than in the case of octamethyl ether (II) [Si···Si 9.812 (4) Å]. In addition, the absence of substituents appears to allow tetraphenylsilane (III) to generate a structure in which each molecule has a larger number of neighbors in contact (14) than in the structure of the corresponding octamethyl ether, (II) (10).

A noteworthy feature of the structure of (II) is the preference of each 3,5-dimethoxyphenyl group for an *anti*,*anti* (*AA*) conformation, (IV), in which the C and O atoms of each methoxy group lie close to the phenyl plane. The alternative planar *anti*,*syn* (*AS*) conformation, (V), and *syn*,*syn* (*SS*) conformation, (VI), are not observed. Analysis of all 47 structures in the Cambridge Structural Database (Version 5.26 of February 2005; Allen, 2002) containing one or more 1-substituted-3,5-dimethoxyphenyl groups revealed that only 20.2% of the units share the observed preference of compound (II) for the *AA* conformation (IV), 14.1% favor the *SS* conformation (VI), and a large majority (64.6%) adopt the *AS* conformation (V).

Together, our observations show that the resorcinol derivative, (I), which has a surface rich in groups that can associate by hydrogen bonding, tends to form open networks, whereas analogs that lack this special feature crystallize as close-packed structures. These differences underscore the importance of suitably oriented hydrogen-bonding groups as directors of crystallization.

## Experimental

Tetrakis(3,5-dimethoxyphenyl)silane, (II), was prepared by the reported method of Saied *et al.* (2005). Crystals were grown by slow evaporation of a solution in $CH_2Cl_2$.

### *Crystal data*

$C_{32}H_{36}O_8Si$
$M_r = 576.70$
Tetragonal, $I4_1/a$
$a = 17.230$ (7) Å
$c = 9.812$ (4) Å
$V = 2913$ (2) Å$^3$
$Z = 4$
$D_x = 1.315$ Mg m$^{-3}$
Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 20.0$–22.5°
$\mu = 1.14$ mm$^{-1}$
$T = 292$ (2) K
Block, colorless
0.72 × 0.15 × 0.12 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: integration (ABSORP in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.760$, $T_{max} = 0.880$
10945 measured reflections
1377 independent reflections
1138 reflections with $I > 2\sigma(I)$
$R_{int} = 0.077$
$\theta_{max} = 69.7°$
$h = -21 \rightarrow 21$
$k = -21 \rightarrow 21$
$l = -11 \rightarrow 11$
5 standard reflections
frequency: 60 min
intensity decay: 0.3%

*Acta Cryst.* (2005). E**61**, o2563–o2566 Saied *et al.* · $C_{32}H_{36}O_8Si$ **o2565**

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.149$
$S = 1.06$
1377 reflections
130 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{min} = -0.36$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0013 (3)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Si—C1$^{i}$ | 1.881 (2) | O5—C51 | 1.424 (3) |
| Si—C1$^{ii}$ | 1.881 (2) | C1—C6 | 1.395 (3) |
| Si—C1 | 1.881 (2) | C1—C2 | 1.398 (3) |
| Si—C1 | 1.881 (2) | C2—C3 | 1.399 (3) |
| O3—C3 | 1.360 (2) | C3—C4 | 1.379 (3) |
| O3—C31 | 1.410 (3) | C4—C5 | 1.383 (3) |
| O5—C5 | 1.366 (2) | C5—C6 | 1.392 (3) |
| | | | |
| C1—Si—C1$^{i}$ | 109.38 (12) | C2—C1—Si | 119.67 (15) |
| C1—Si—C1$^{ii}$ | 109.52 (6) | C1—C2—C3 | 119.66 (19) |
| C1$^{i}$—Si—C1$^{ii}$ | 109.52 (6) | O3—C3—C4 | 115.16 (18) |
| C1—Si—C1 | 109.52 (6) | O3—C3—C2 | 124.4 (2) |
| C1$^{i}$—Si—C1 | 109.52 (6) | C4—C3—C2 | 120.41 (18) |
| C1$^{ii}$—Si—C1 | 109.38 (12) | C3—C4—C5 | 119.90 (18) |
| C3—O3—C31 | 118.33 (19) | O5—C5—C4 | 114.76 (17) |
| C5—O5—C51 | 118.06 (17) | O5—C5—C6 | 124.62 (18) |
| C6—C1—C2 | 119.57 (18) | C4—C5—C6 | 120.62 (19) |
| C6—C1—Si | 120.65 (14) | C5—C6—C1 | 119.82 (18) |
| | | | |
| C1$^{i}$—Si—C1—C6 | −81.85 (12) | C1—C2—C3—C4 | −1.1 (3) |
| C1$^{ii}$—Si—C1—C6 | 38.18 (13) | O3—C3—C4—C5 | −179.82 (19) |
| C1—Si—C1—C6 | 158.20 (16) | C2—C3—C4—C5 | 0.1 (3) |
| C1$^{i}$—Si—C1—C2 | 94.3 (2) | C51—O5—C5—C4 | 178.4 (2) |
| C1$^{ii}$—Si—C1—C2 | −145.63 (18) | C51—O5—C5—C6 | −0.5 (3) |
| C1—Si—C1—C2 | −25.60 (17) | C3—C4—C5—O5 | −178.07 (18) |
| C6—C1—C2—C3 | 1.1 (3) | C3—C4—C5—C6 | 0.9 (3) |
| Si—C1—C2—C3 | −175.13 (15) | O5—C5—C6—C1 | 177.98 (18) |
| C31—O3—C3—C4 | −174.6 (2) | C4—C5—C6—C1 | −0.9 (3) |
| C31—O3—C3—C2 | 5.5 (4) | C2—C1—C6—C5 | −0.1 (3) |
| C1—C2—C3—O3 | 178.81 (19) | Si—C1—C6—C5 | 176.07 (14) |

Symmetry codes: (i) $-y+\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$; (ii) $-x, -y+\frac{1}{2}, z$.

The Si atom was located at a site of $\overline{4}$ symmetry. H atoms were located in a Fourier difference map and refined with isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: modified version of *NRC-2*/*NRC2A* (Ahmed *et al.*, 1973); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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