

H atoms were placed geometrically and allowed to ride on their parent atoms. Residual electron density of  $ca\ 0.3\ e\ \text{\AA}^{-3}$  near the C2 atom may indicate a very small degree of disorder.

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1232). Services for accessing these data are described at the back of the journal.

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## A Triclinic Polymorph of Hexaphenylcyclotrisiloxane

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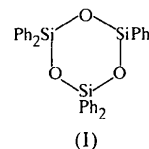
(Received 21 January 1998; accepted 23 February 1998)

## Abstract

In triclinic crystals of 2,2,4,4,6,6-hexaphenylcyclotrisiloxane,  $C_{36}H_{30}O_3Si_3$ , the endocyclic C—C—C bond angles in the phenyl groups at the C atoms bound to silicon are reduced to about  $117^\circ$ . The other geometric parameters do not show any significant differences from expected values.

## Comment

Crystals of the title compound, (I), a large scale precursor in silicone chemistry, were first prepared and investigated by Hyde *et al.* (1947). Two kinds of crystals were optically separated and were characterized as orthorhombic and triclinic polymorphs by X-ray powder diffraction. The structure of the orthorhombic polymorph was later determined by Bokii *et al.* (1972) and redetermined with higher precision by Tomlins *et al.* (1985). The redetermination revealed small but significant distortions of the phenyl rings from their ideal geometry. With the intention of generating diphenylsilanediol by reaction of dichlorodiphenylsilane with water in toluene in the presence of *tert*-amyl alcohol (Burkhard, 1945), hexaphenylcyclotrisiloxane, (I), was formed after the solution had been stored for more than two weeks at room temperature. The solid was recrystallized from warm 2-butanone and chloroform as large colorless blocks.



The present structure analysis of the triclinic polymorph also shows some significant distortions of the phenyl rings, most significantly, the decrease of the C—C—C bond angles to  $117.0(4)^\circ$  at those phenyl C atoms bound at silicon. A similar distortion observed in the structure of 2,2-diphenyl-2-sila-1,3,4-trihydro-

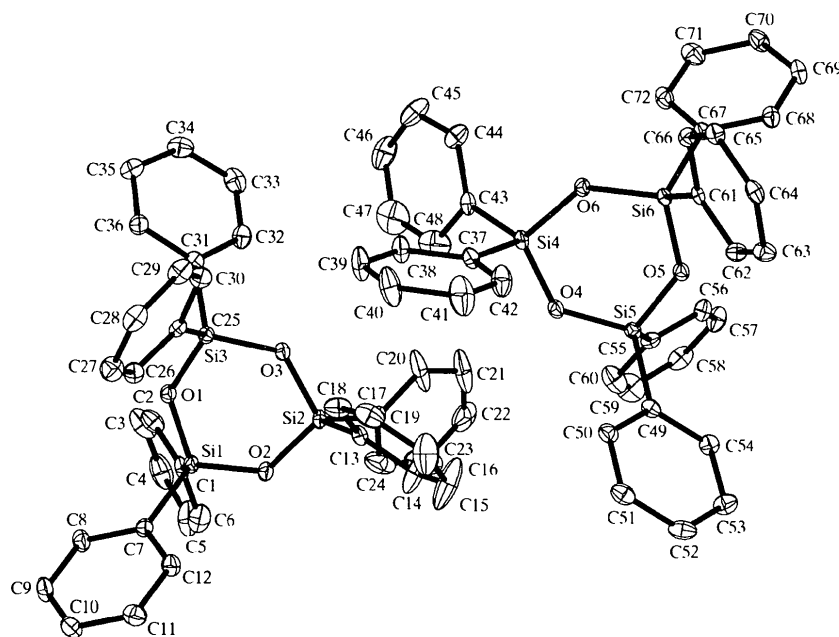


Fig. 1. The molecular structures of the two molecules of the title compound showing 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

naphthalene has already been discussed by Domenicano *et al.* (1975). However, we cannot confirm the *M* effect of the silicon discussed by Tomlins *et al.* (1985). In contrast to a shortening of the C—C bonds in the 2,3- and 5,6-positions, we found only a slight shortening of the bonds in the 3,4 and 4,5-positions. The two independent molecules in the asymmetric part of the unit cell and the numbering scheme are shown in Fig. 1. Both molecules have nearly identical geometry in the central Si—O rings, as well as in the phenyl ligands. Except for the Si—O—Si angles, which are in the range 131.21 (8)–131.84 (8)° in the first molecule and 132.13 (7)–132.73 (8)° in the second molecule, all other corresponding bond lengths and angles are equal within 1 $\sigma$ .

## Experimental

Slow hydrolysis of dichlorodisilane in toluene–water in the presence of *tert*-amyl alcohol normally leads to diphenylsilanediol in excellent yield (Burkhard, 1945). A condensation reaction, catalyzed by the formed hydrochloric acid, however, generates hexaphenylcyclotrisiloxane during the storage of the silanediol solution over a period of two weeks or longer. Colorless clear blocks could be separated from solution and were recrystallized from a warm mixture of 2-butanone and chloroform (1:1). The melting point was determined as 464 K. The results of elemental analysis, as well as of proton, <sup>13</sup>C, <sup>29</sup>Si NMR, and IR spectroscopy, confirm the determined structure.

### Crystal data

C<sub>36</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>  
M<sub>r</sub> = 594.93

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å

### Triclinic

*P* $\bar{1}$

*a* = 12.870 (2) Å

*b* = 15.060 (2) Å

*c* = 16.575 (2) Å

$\alpha$  = 84.07 (2)°

$\beta$  = 84.122 (15)°

$\gamma$  = 77.77 (2)°

*V* = 3112.0 (8) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.270 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

### Data collection

Stoe IPDS diffractometer

$\varphi$  rotation scans (157

exposures with  $\varphi_{\text{incr}}$  =  
1.4°)

Absorption correction: none

27 194 measured reflections

10 745 independent  
reflections

### Refinement

Refinement on *F*<sup>2</sup>

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.097$

*S* = 0.932

10 735 reflections

997 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 5000  
reflections

$\theta$  = 2.5–25.2°

$\mu$  = 0.188 mm<sup>-1</sup>

*T* = 150 (2) K

Prism

0.60 × 0.55 × 0.44 mm

Colorless

8067 reflections with  
*I* > 2 $\sigma$ (*I*)

*R*<sub>int</sub> = 0.071

$\theta_{\text{max}}$  = 25.35°

*h* = -15 → 15

*k* = -18 → 18

*l* = -19 → 19

Intensity decay: none

( $\Delta/\sigma$ )<sub>max</sub> = -0.014

$\Delta\rho_{\text{max}}$  = 0.409 e Å<sup>-3</sup>

$\Delta\rho_{\text{min}}$  = -0.278 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected bond angles (°)

C2—C1—C6	117.2 (2)	C42—C37—C38	117.3 (2)
C12—C7—C8	117.4 (2)	C48—C43—C44	117.0 (2)
C18—C13—C14	115.9 (2)	C54—C49—C50	117.3 (2)
C24—C19—C20	116.8 (2)	C56—C55—C60	117.5 (2)
C26—C25—C30	117.7 (2)	C62—C61—C66	117.6 (2)
C36—C31—C32	117.3 (2)	C72—C67—C68	117.6 (2)

Atoms C15 and C23 reveal very anisotropic atomic displacement parameters. However, introducing split sites for these atoms did not improve the refinement results. All criteria of quality such as *R* values, goodness-of-fit and final difference electron-density residues became worse.

Data collection: *IPDS* (Stoe & Cie, 1997*a*). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XSTEP* (Stoe & Cie, (1997*b*)). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1181). Services for accessing these data are described at the back of the journal.

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## 2,6-Dibromo-4-nitroaniline

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### Abstract

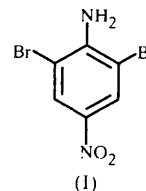
In the crystal structure of 2,6-dibromo-4-nitroaniline, C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, weak hydrogen bonds exist between the pair of amino protons on one molecule and the

pair of *p*-nitro O atoms on an adjacent molecule, with further interactions, perpendicular to these weak hydrogen bonds, between O and Br atoms on neighbouring molecules, forming  $\pi$ -stacked two-dimensional layers in the crystallographic *a* direction.

### Comment

The molecular structures of substituted benzene derivatives have aroused much interest because of potential non-linear optical properties. In particular, nitroaniline derivatives comprise both electron-donating amine and electron-withdrawing nitro groups and exhibit intriguing three-dimensional arrays with extensive hydrogen bonding. Molecules of this type are often observed to form infinite polar chains linked by intermolecular hydrogen bonding between amine H and nitro O atoms on neighbouring molecules. Extensive studies have been undertaken on hydrogen bonding in nitroaniline derivatives (Etter *et al.*, 1987) and it has been found that the most common bonding mode, often referred to as the primary interaction, involves a three-centre interaction with one proton of the amino group located between the two 'inside' lone pairs of electrons of a single nitro group. In primary amines, this leaves a second amine proton to hydrogen bond either intramolecularly to *ortho* substituents or intermolecularly to other molecules. Such interactions are observed in nitroaniline (Tonogaki *et al.*, 1993), 2-methyl-4-nitroaniline (Garito *et al.*, 1981), 2,6-dichloro-4-nitroaniline (Hughes & Trotter, 1971), as well as in secondary amines such as *N*-methyl-4-nitroaniline (Butcher *et al.*, 1992). Much less common is the hydrogen-bonding mode in which both amine protons are involved in hydrogen bonding to one nitro group on a neighbouring molecule. This rare type of interaction is observed in 3-trifluoromethyl-2,4,6-trinitroaniline (Butcher *et al.*, 1992). Substituents on the nitroaniline allow further intermolecular interactions. Hydroxy and halide groups, in particular, may contribute to intermolecular bonding in the crystal structure.

The crystal structure of 2,6-dibromo-4-nitroaniline, (I), provides another example of the less common paired-hydrogen-bonding mode in which both amine



protons on one molecule interact with a nitro group of a neighbouring molecule. These interactions link the molecules in a linear polar chain, as shown in Fig. 1, which lies astride a crystallographic mirror plane. The hydrogen-bond contacts are of typical lengths for primary amines [N···O 2.941 (9) and N—H···O 2.334 (9) Å].