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Stereoelectronic Effects in the Si−C Bond: A Study of the Molecular Structure and Conformation of Tetraphenylsilane by Gas-Phase Electron Diffraction and Theoretical Calculations

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The molecular structure and conformation of tetraphenylsilane have been investigated by gas-phase electron diffraction and ab initio/DFT and molecular mechanics calculations. The structure of the free molecule is consistent with an S_4 symmetry conformation; the calculations indicate that the twist angle τ between the plane of the phenyl group and the plane defined by the Si−C bond and the S_4 axis is about 40°. Analysis of the low-frequency modes indicates that the four phenyl groups undergo large-amplitude torsional and bending vibrations about the respective Si−C bonds. The electron diffraction intensities from a previous study [Csákvári, É.; Shishkov, I. F.; Rozsondai, B.; Hargittai, I. *J. Mol. Struct.* **1990**, *239*, 291] have been reanalyzed, using constraints from the calculations. A dynamical model accounting for the large-amplitude bending motion of the phenyl groups was used in the refinement. The new analysis yields accurate values for the twist angle of the phenyl group, $\tau = 40 \pm 2°$, and the Si−Ph bond length, $r_g = 1.881 \pm 0.004$ Å. The Si−Ph bond in tetraphenylsilane is marginally longer than the Si−Me bond in tetramethylsilane, $r_g = 1.877 \pm 0.004$ Å from the analysis of electron diffraction data taken with the same apparatus. This contrasts with chemical expectation, which would suggest a difference of 0.03 Å in the opposite sense, based on the covalent radii of C(sp^3) and C(sp^2). A delicate balance of subtle stereoelectronic effects, involving electron delocalization into the σ^*(Si−C) and 3d(Si) orbitals, appears to be responsible for the nearly equal length of the Si−C bonds in the two molecules. Other bond lengths from the present electron diffraction study are $\langle r_g(\mathrm{C-C})\rangle = 1.401 \pm 0.003$ Å and $\langle r_g(\mathrm{C-H})\rangle = 1.102 \pm 0.003$ Å. The ipso ring angle of the phenyl groups is 117.5° from the DFT calculations, in close agreement with solid-state results.

Introduction

The length of the Si−C bond in organosilicon compounds is sensitive to the chemical environment.[1] Our experimental and computational studies of the molecular structures of phenyltrimethylsilane[2] and *p*-bis(trimethylsilyl)benzene[3] have shown that the difference in the lengths of the Si−Me and Si−Ph bonds is surprisingly small, a few thousandths of an ångstrom at most. This is in contrast with chemical expectation, which would suggest a difference of about 0.03 Å, based on the covalent radii of C(sp^3) and C(sp^2).[4]

To obtain conclusive evidence on this point we need accurate gas-phase electron diffraction studies of molecules containing only one type of Si−C bond, and, preferably, based on experimental data from the same laboratory to minimize systematic errors. We have recently investigated the gas-phase structure of tetramethylsilane;[5] here we report a detailed study of the molecular structure of tetraphenylsilane, based on electron diffraction intensities from a previous study[6] and augmented by molecular orbital (MO) and molecular mechanics (MM) calculations. The use of important constraints from the theoretical calculations has substantially improved the accuracy of the experimental study.

The conformation of tetraphenylsilane was studied extensively by empirical calculations. Kitaigorodsky and co-workers[7] used atom−atom potentials to determine the conformation of the molecule in the gaseous phase and in the crystal; Mislow and co-workers[8] investigated the free molecule by force-field calculations. These studies have shown that the free molecule has S_4 symmetry, with a twist angle τ (defined as the dihedral angle between the plane of the benzene ring and the plane formed by the Si−C bond and the S_4 axis) close to 40°. The crystal structure of tetraphenylsilane has been studied repeatedly;[9−12] the molecule has S_4 crystallographic symmetry, with a twist angle τ close to 51°, the value anticipated by Kitaigorodsky’s calculations.[7]

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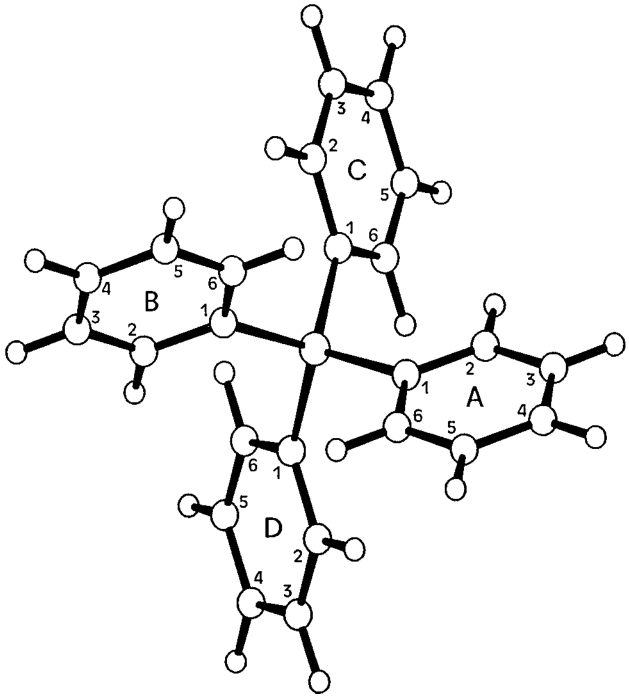

Figure 1. Numbering of atoms in tetraphenylsilane.

Theoretical Calculations

The free molecule was assumed to have S_4 symmetry. Models of D_{2d} symmetry, with the phenyl groups either perpendicular to or lying in the plane defined by the respective Si−Ph bond and the S_4 axis, were also considered. They correspond to first-order saddle points on the potential energy surface.

Ab initio/DFT calculations were carried out using the *Gaussian 98* package.[13] The geometry of the molecule was first optimized[14] at the Hartree−Fock (HF) level with the 6-31G* basis set.[15] The stationary points were then characterized by harmonic normal-mode analysis. Further geometry optimizations were carried out with Becke's three-parameter hybrid HF/DFT method,[16] using Lee−Yang−Parr's correlational functional (B3LYP).[17] Apart from the symmetry constraints, geometry optimization was otherwise complete. The optimized equilibrium geometry of tetraphenylsilane is reported in Table 1; the numbering of atoms is shown in Figure 1. The relative energies of the equilibrium S_4 and the D_{2d} conformations of the molecule are reported in Table 2.

The MM calculations were carried out with the MM3 force field.[18] They provided vibrational frequencies and energy differences between the S_4 and D_{2d} conformations and vibrational amplitudes for the electron diffraction least-squares refinement.

Calculated low-frequency modes ($\tilde{\nu} < 160$ cm^{-1}) for the equilibrium conformation of the molecule are identified in Table 3. Their analysis shows that the four phenyl groups are not only involved in torsional motions but also undergo large-amplitude bending motions from the respective Si−C bonds.

All calculations were run on an Alpha AXP-3000/500 cluster at the University of Rome "La Sapienza".

Electron Diffraction Study

The analysis was based on the electron diffraction intensities from the previous study (nozzle temperature of 573 K).[6] The data used had $2.000 \leq s \leq 13.500$ Å^{-1} (50 cm camera distance) and $9.25 \leq s \leq 35.50$ Å^{-1} (19 cm camera distance), with data intervals of 0.125 and 0.25 Å^{-1}, respectively.

TABLE 1: Equilibrium Molecular Geometry of Tetraphenylsilane (S_4 Symmetry) from MO Calculations

parameter	HF/6-31G*	B3LYP/6-31G*
Bond Distances (Å)		
r(Si−C1)	1.896_6	1.894_1
r(C1−C2)	1.396_0	1.406_9
r(C2−C3)	1.386_7	1.396_2
r(C3−C4)	1.384_3	1.395_6
r(C4−C5)	1.386_1	1.396_1
r(C5−C6)	1.384_9	1.396_0
r(C1−C6)	1.398_9	1.408_8
$\langle r$(C−C)$\rangle$	1.389_5	1.399_9
r(C2−H2)	1.074_9	1.087_1
r(C3−H3)	1.075_7	1.087_2
r(C4−H4)	1.075_7	1.087_1
r(C5−H5)	1.075_8	1.087_2
r(C6−H6)	1.076_2	1.087_8
Angles (degrees)		
∠C1A−Si−C1B	108.1_6	108.6_4
∠C1A−Si−C1C	110.1_3	109.8_9
∠Si−C1−C2	121.9_0	121.5_3
∠Si−C1−C6	120.7_1	120.9_1
∠C2−C1−C6	117.3_8	117.5_4
∠C1−C2−C3	121.4_2	121.3_4
∠C2−C3−C4	120.0_7	120.0_8
∠C3−C4−C5	119.6_7	119.6_7
∠C4−C5−C6	119.9_6	120.0_1
∠C1−C6−C5	121.5_0	121.3_6
∠C1−C2−H2	119.8_9	119.6_5
∠C3−C2−H2	118.6_9	119.0_1
∠C2−C3−H3	119.8_4	119.8_5
∠C4−C3−H3	120.0_9	120.0_7
∠C3−C4−H4	120.1_8	120.1_8
∠C5−C4−H4	120.1_4	120.1_5
∠C4−C5−H5	120.1_3	120.1_0
∠C6−C5−H5	119.9_2	119.8_9
∠C5−C6−H6	118.6_6	118.8_5
∠C1−C6−H6	119.8_4	119.7_8
Torsion Angles (degrees)		
C2A−C1A−Si−C1B	−140.3	−142.2
C6A−C1A−Si−C1B	40.9	39.7
C2A−C1A−Si−C1C	−19.9	−21.9
C6A−C1A−Si−C1C	161.3	160.0
C2A−C1A−Si−C1D	99.3	97.6
C6A−C1A−Si−C1D	−79.5	−80.6
Displacements (Å) from the Least-Squares Plane through the C Atoms of the Phenyl Group		
C1A	−0.003	−0.003
C2A	.001	.001
C3A	.001	.001
C4A	−0.002	−0.002
C5A	.000	.000
C6A	.002	.002
Si	−0.048	−0.065
C1B	1.104	1.040
C1C	.524	.550
C1D	−1.817	−1.846
H2A	.012	.011
H3A	.006	.007
H4A	.000	.000
H5A	.004	.004
H6A	.017	.019
Dihedral Angles (degrees) between the Least-Squares Plane through the C Atoms of Phenyl Group A and the C−Si−C Planes		
Plane through		
C1A, Si, C1B	40.4	38.9
C1A, Si, C1C	19.3	21.0
C1A, Si, C1D	80.1	81.5

The least-squares method was applied to molecular intensities according to our normal procedure,[20] using a modified version of the program by Seip and co-workers.[21] The inelastic and elastic scattering functions were taken from refs 22 and 23,

TABLE 2: Relative Energies of the S_4 and D_{2d} Conformations of Tetraphenylsilane from Theoretical Calculations

	relative energy (kJ mol^{-1})		
conformation	MM3	HF/6-31G*	B3LYP/6-31G*
S_4 (equilibrium)	0.0	0.0	0.0
D_{2d} ($\tau = 0°$)[a]	44.8	50.5	-
D_{2d} ($\tau = 90°$)[a]	4.4	10.2	8.1

[a] Dihedral angle between the plane of the benzene ring and the plane defined by the Si−C bond and the S_4 axis.

TABLE 3: Low-Frequency Vibrational Modes ($\tilde{\nu} < 160$ cm^{-1}) for the Equilibrium Conformation of Tetraphenylsilane (S_4 Symmetry) from Theoretical Calculations

	wavenumber (cm^{-1})		
symmetry	B3LYP/6-31G*	MM3	IR intensity[a]
A	32.2	29.0	inactive
E	32.3	28.6	vw
B	38.7	36.7	vw
B	54.6	59.8	vw
A	54.6	54.5	inactive
E	57.2	58.9	vw
B	65.4	62.0	vw

[a] The far IR spectrum in benzene solution is reported[19] to be free of bands between 20 and 150 cm^{-1}.

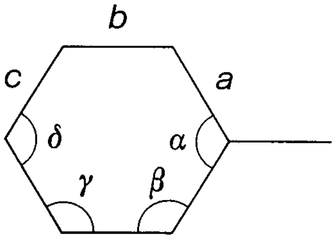

Figure 2. Lettering of bond distances and angles in a monosubstituted benzene ring of C_{2v} symmetry.

respectively. The initial background lines were modified repeatedly in the course of the analysis.

The molecule was assumed to adopt a conformation of S_4 symmetry; the C_6H_5−Si fragments were imposed C_{2v} local symmetry. The C−H bonds were represented by a mean length, and each was assumed to bisect the corresponding C−C−C angle, as in our previous studies of monosubstituted benzene derivatives.[24] Under these constraints the geometry of the molecule is described by nine independent parameters, which were chosen as follows (see Figures 1 and 2): (i) three bond distances, r(Si−C1), r(C1−C2), and $\langle r(\text{C−H})\rangle$; (ii) two differences between bond distances, Δ_1(C−C) = r(C1−C2) − r(C2−C3) = $a - b$ and Δ_2(C−C) = r(C2−C3) − r(C3−C4) = $b - c$; (iii) three bond angles, ∠C1A−Si−C1B, ∠C2−C1−C6 = α, and ∠C1−C2−C3 = β; and (iv) the twist angle of the phenyl group, τ, defined as the dihedral angle between the plane of the ring and the plane defined by the Si−C1 bond and the S_4 axis.

The lowering of symmetry at the Si atom from T_d to S_4, due to the C_{2v} local symmetry of the phenyl groups, causes the six tetrahedral C−Si−C angles to split into two groups. MM and MO calculations consistently indicate that the angle C1A−Si−C1B (where C1A and C1B are related by the 2-fold axis contained in S_4) is up to two degrees smaller than ∠C1A−Si−C1C. This small difference makes the bond angles at Si hard to determine accurately by electron diffraction. We eventually found appropriate to assume ∠C1A−Si−C1B at its calculated (B3LYP) value, 108.6$_4$°. The assumption of slightly different values within a one-degree range in either direction was tested and found to have no appreciable effect on the other molecular parameters, with the exception of the twist angle τ, which decreases by 3° when ∠C1A−Si−C1B is increased by 1°.

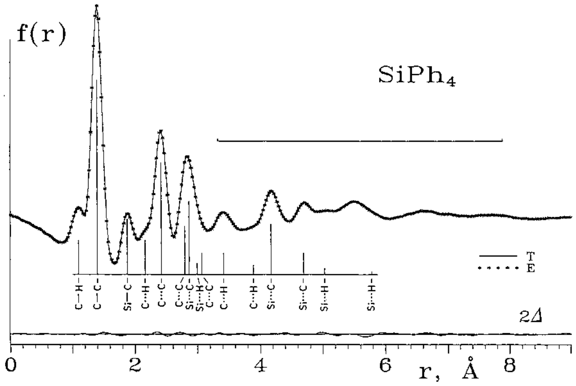

Figure 3. Radial distribution curves (E, experimental; T, theoretical). They were calculated using an artificial damping factor exp(−0.002s^2); theoretical values were used in the $0.00 \leq s \leq 1.75$ Å^{-1} region. The positions of the most important conformation-independent distances are marked with vertical bars, whose heights are proportional to the relative weights of the atom pairs. The region where contributions from conformation-dependent C···C distances occur is indicated by a horizontal line. Also shown is the difference curve (E − T).

The three different bond distances and four different angles of the benzene ring (Figure 2) are linked by two equations of geometrical constraint, expressing the conditions of planarity and ring closure.[25] Thus only five independent parameters are required to define the ring geometry. The differences $a - b$ and $b - c$ are too small to be determined accurately by electron diffraction and were assumed from the B3LYP calculations. The angle β was assumed to be linearly related to α, according to the empirical relationship $\Delta\beta = -0.6052\ \Delta\alpha - 0.084°$ (where Δα and $\Delta\beta$ are deviations from 120°).[26]

The large-amplitude bending motions of the phenyl groups are expected to cause an apparent shortening of all Si···C and Si···H distances, resulting in a systematic distortion of the geometry of the molecule. This effect was treated by allowing the four phenyl groups to bend from the respective Si−C1 bonds by equal amounts, with the plane through Si, C1, and C4 remaining perpendicular to the plane of the ring. A shrinkage parameter θ, defined as the effective bending angle of the Si−C1 bond from the C1···C4 line, was refined as an independent variable.

Ten mean amplitudes of vibration, l, were also refined as independent variables. They were coupled in groups to other amplitudes with constrained differences, Δl. These differences and other fixed amplitudes were taken from spectroscopic calculations based on the MM3 force field.[18]

Important molecular parameters from the final refinement are reported in Table 4, showing also the coupling of the vibrational amplitudes.[27] Experimental and calculated radial distributions are shown in Figure 3. Total experimental intensities are collected in Table 1S (Supporting Information; see the supporting information paragraph at the end of the paper).

Results and Discussion

The geometrical parameters of tetraphenylsilane from the present electron diffraction study are compared with those from the previous study[6] and the B3LYP MO calculations in Table 5.

Molecular Conformation. The present experimental and theoretical studies consistently indicate that free tetraphenylsi-

TABLE 4: Molecular Parameters of Tetraphenylsilane from Electron Diffraction[a]

			l		
atom pair	multiplicity	r_a	exp.	calc.[c]	coupling scheme[d]
Distances and Mean Amplitudes of Vibration[b] (Å)					
C1−C2	8	1.4073(1)	0.0488(2)	0.047	i
C2−C3	8	1.3955(1)[e]	0.0488	0.047	i
C3−C4	8	1.3953(1)[e]	0.0488	0.047	i
Si−C1	4	1.8783(7)	0.0644(7)	0.059	ii
⟨C−H⟩	20	1.097(1)	0.076(1)	0.077	iii
C1···C3	8	2.4443(2)[e]	0.0627(3)	0.063	iv
C1···C4	4	2.8240(2)[e]	0.0771(6)	0.072	v
C2···C4	8	2.4155(2)[e]	0.0627	0.063	iv
C2···C5	8	2.7857(2)[e]	0.0771	0.072	v
C2···C6	4	2.4067(2)[e]	0.0637	0.064	iv
C3···C5	4	2.4152(2)[e]	0.0627	0.063	iv
Si···C2	8	2.8671(6)[e]	0.0981	0.093	v
Si···C3	8	4.171(1)[e]	0.095(1)	0.089	vi
Si···C4	4	4.690(1)[e]	0.091(2)	0.085	vii
C1···H2	8	2.166(1)[e]	0.104(1)	0.102	viii
C1···H3	8	3.434(1)[e]	0.103	0.101	viii
C1···H4	4	3.921(1)[e]	0.104	0.102	viii
C2···H3	8	2.164(1)[e]	0.104	0.102	viii
C2···H4	8	3.410(1)[e]	0.103	0.101	viii
C2···H5	8	3.882(1)[e]	0.104	0.102	viii
C2···H6	8	3.404(1)[e]	0.103	0.101	viii
C3···H2	8	2.156(1)[e]	0.103	0.101	viii
C3···H4	8	2.164(1)[e]	0.104	0.102	viii
C3···H5	8	3.410(1)[e]	0.103	0.101	viii
C3···H6	8	3.882(1)[e]	0.104	0.102	viii
C4···H2	8	3.405(1)[e]	0.103	0.101	viii
C4···H3	8	2.164(1)[e]	0.104	0.102	viii
Si···H2	8	2.9879(6)[e]	0.166[f]	0.166	
Si···H3	8	5.025(1)[e]	0.134[f]	0.134	
Si···H4	4	5.785(2)[e]	0.112[f]	0.112	
C1A···C1B	2	3.051(1)[e]	0.113(4)	0.128	ix
C1A···C2B	4	4.267(6)[e]	0.181	0.196	ix
C1A···C6B	4	3.407(7)[e]	0.201	0.216	ix
C1A···C1C	4	3.075(1)[e]	0.129(4)	0.125	x
C1A···C2C	4	3.975(9)[e]	0.298	0.294	x
C1A···C6C	4	3.797(10)[e]	0.227	0.223	x
C1A···C2D	4	3.335(4)[e]	0.212	0.208	x
C1A···C6D	4	4.371(3)[e]	0.136	0.132	x
Angles (degrees)					
∠C2−C1−C6 (α)	117.54[g]				
∠C1−C2−C3 (*β*)	121.41[e]				
∠C2−C3−C4 (*γ*)	119.88[e]				
∠C3−C4−C5 (*δ*)	119.88[e]				
∠C1A−Si−C1B	108.64[g]				
∠C1A−Si−C1C	109.89[e]				
τ[h]	39.6(10)				
θ[i]	8.4(5)				
Differences between Bond Distances (Å)					
Δ_1(C−C)[j]	0.0118[g]				
Δ_2(C−C)[k]	0.0002[g]				

[a] Least-squares standard deviations are given in parentheses as units in the last digit. They should be considered merely as indicators of internal consistency, and are sometimes unrealistically small due to the constraints employed in the refinement. [b] To economize on space, the table includes only a few of the 57 independent inter-ring C···C pairs. Their distances range from 3.05 to 7.90 Å, and their amplitudes (which were refined in two large blocks with constrained differences) from 0.113 to 0.592 Å. Also excluded are the 90 independent inter-ring C···H pairs. [c] From MM calculations (MM3 force field). [d] The roman numerals indicate the groups within which the amplitudes were refined with constant differences between them. [e] Dependent parameter. [f] Assumed from the MM3 calulations. [g] Assumed from the B3LYP calculations. [h] Dihedral angle between the plane of the benzene ring and the plane defined by the Si−C bond and the S_4 axis. [i] Effective bending angle of the Si−C1 bond from the C1···C4 line, in a plane perpendicular to the plane of the ring. [j] Δ_1(C−C) = *r*(C1−C2) − *r*(C2−C3). [k] Δ_2(C−C) = *r*(C2−C3) − *r*(C3−C4).

TABLE 5: Molecular Geometry[a] **of Tetraphenylsilane: Comparison of Experimental and Theoretical Results**

	electron diffraction[b]		B3LYP/6-31G*
parameter	reference 6[d]	this work[e]	calculations[c]
r(Si−C)	1.871 ± 0.004	1.881 ± 0.004	1.894
⟨*r*(C−C)⟩	1.403 ± 0.003	1.401 ± 0.003	1.400
r(C1−C2)	1.399[f,g]	1.409[h]	1.408
r(C2−C3)	1.404[f,g]	1.397[h]	1.396
r(C3−C4)	1.404[f,g]	1.397[h]	1.396
⟨*r*(C−H)⟩	1.087 ± 0.004	1.102 ± 0.003	1.087
∠C1A−Si−C1B	112.3(4)	108.6[i]	108.6
∠C1A−Si−C1C	108.1(2)[j]	109.9[j]	109.9
∠C2−C1−C6 (α)	118.2 ± 0.4	117.5[i]	117.5
∠C1−C2−C3 (*β*)	121.3(2)[j]	121.4[j]	121.4
∠C2−C3−C4 (*γ*)	120.0[k]	119.9[j]	120.0
∠C3−C4−C5 (*δ*)	119.2(2)[j]	119.9[j]	119.7
τ[l]	could not be determined reliably	40 ± 2°	38.9

[a] Bond distances are given in Å, angles in degrees. [b] Bond distances are r_g values. [c] Bond distances are r_e values. Whenever necessary, bond distances and angles have been averaged to be consistent with the symmetry constraints adopted in the electron diffraction studies. [d] Estimated total errors are given as error limits; least-squares standard deviations are given in parentheses as units in the last digit. [e] Total errors are given as error limits. They were estimated as $\sigma_T = [2\sigma_{LS}^2 + (0.002r)^2 + (\Delta/2)^2]^{1/2}$ (for bond distances) and $\sigma_T = [2\sigma_{LS}^2 + (\Delta/2)^2]^{1/2}$ (for angles), where σ_{LS} is the least-squares standard deviation, and Δ/2 is the effect of the constraints adopted in the refinement.[28] [f] The difference *r*(C1−C2) − *r*(C2−C3) was refined as an independent variable; the difference *r*(C2−C3) − *r*(C3−C4) was set equal to 0. [g] Calculated from the structural parameters given in Table 2, column 5, of ref 6. [h] The differences *r*(C1−C2) − *r*(C2−C3) and *r*(C2−C3) − *r*(C3−C4) have been assumed from the B3LYP calculations. [i] Assumed from the B3LYP calculations. [j] Derived parameter. [k] Assumed. [l] Dihedral angle between the plane of the benzene ring and the plane defined by the Si−C bond and the S_4 axis.

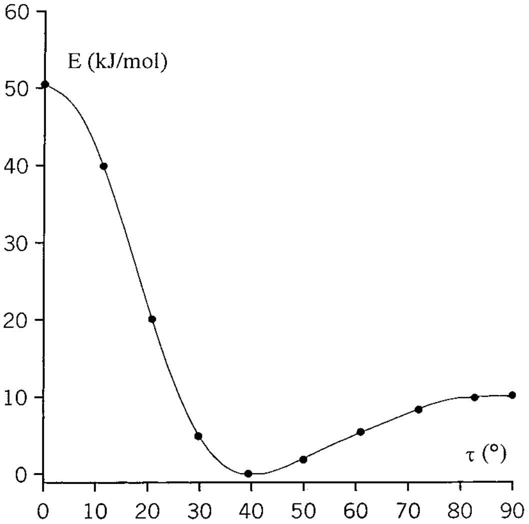

Figure 4. Plot of the potential energy of tetraphenylsilane, calculated at the HF/6-31G* level assuming S_4 symmetry, against the twist angle of the phenyl group, *τ*.[29] The conformations with *τ* = 0° and *τ* = 90° have D_{2d} symmetry.

lane has a minimum-energy conformation of S_4 symmetry, with a twist angle *τ* of about 40°. This confirms the results of empirical calculations.[7,8] The potential energy of a tetraphenylsilane molecule of S_4 symmetry, calculated at the HF/6-31G* level, is plotted against the twist angle *τ* in Figure 4.[29] The molecule attains its highest possible symmetry, D_{2d}, when *τ* = 0° or 90°. These conformations correspond to first-order saddle points, separating two equivalent energy minima. The saddle point at *τ* = 0° lies about 50 kJ mol^{-1} higher in energy than the minimum, due to particularly short contacts between the

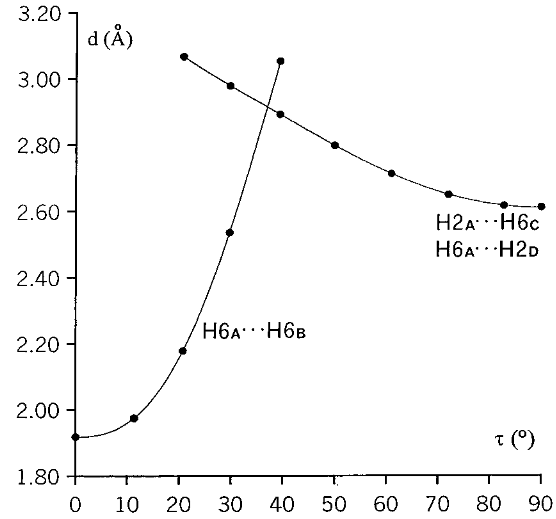

Figure 5. Plot of the shortest inter-ring H···H distances in tetraphenylsilane, calculated at the HF/6-31G* level assuming S_4 symmetry, against the twist angle of the phenyl group, τ.[29]

TABLE 6: Length of the Si−C Bond (Å) in Tetramethylsilane and Tetraphenylsilane: Experimental and MO Results

technique	$SiMe_4$[a]	$SiPh_4$[b]
electron diffraction[c]	1.877 ± 0.004	1.881 ± 0.004
HF/6-31G* calculations[d]	1.894	1.897
B3LYP/6-31G* calculations[d]	1.895	1.894

[a] Reference 5. [b] This work. [c] Bond distances are r_g values. [d] Bond distances are r_e values.

ortho hydrogens. The saddle point at $\tau = 90°$ is much lower in energy and is rather flat. The rationale for the conformation adopted by free tetraphenylsilane is apparent from Figure 5, where the shortest inter-ring H···H distances are plotted against the twist angle τ. In the solid state, the molecule has S_4 crystallographic symmetry with $\tau = 52.4°$ (calculated from the atomic and unit-cell parameters given in the literature).[9,11,12]

The Silicon−Carbon Bond Length. The length of the Si−Ph bond in tetraphenylsilane, $r_g = 1.881 \pm 0.004$ Å,[30] is accurately determined from electron diffraction. Comparison with the length of the Si−Me bond in tetramethylsilane, $r_g = 1.877 \pm 0.004$ Å based on electron diffraction experimental data from the same apparatus,[5] indicates that the two bonds have nearly equal length, in agreement with the theoretical calculations (see Table 6). This contrasts with chemical expectation, which would suggest r(Si−Me) to exceed r(Si−Ph) by about 0.03 Å, based on the covalent radii of C(sp^3), 0.77 Å, and C(sp^2), 0.74 Å.[4]

It should of course be considered that a Si−C bond is weaker than a C−C bond. This is witnessed by the lower bond energy, ca. 300 vs 350 kJ mol^{-1},[31] and smaller stretching force constant, 2.7−3.0 vs 4.5 mdyn $Å^{-1}$.[32,33] Thus, the length of a Si−C bond is more prone to be affected by changes in chemical environment than that of a C−C bond.

It can be ruled out, however, that steric hindrance in the equilibrium conformation of tetraphenylsilane may lengthen the Si−C bond by as much as 0.03 Å. The MO calculations indicate that changing the twist angle τ from the equilibrium value (40.4°) to 0° causes the Si−Ph bond to lengthen only 0.009 Å, notwithstanding the substantial increase in repulsive interactions between phenyl groups (the shortest inter-ring H···H contact becomes 1.92 Å when $\tau = 0°$, see Figure 5).

The nearly equal length of the Si−C bonds in tetramethylsilane and tetraphenylsilane is likely to arise from a delicate balance of subtle stereoelectronic effects. The fully staggered conformation of tetramethylsilane[5] gives rise to a W arrangement of bonds that favors the interaction of the bonding σ(C−H) and σ(Si−C) orbitals with the empty σ^*(Si−C) and σ^*(C−H) orbitals, respectively.[34] Natural bond orbital analysis[35] shows that the $\sigma(\text{C−H})\rightarrow\sigma^*(\text{Si−C})$ delocalization is more pronounced than the $\sigma(\text{Si−C})\rightarrow\sigma^*(\text{C−H})$ delocalization, a consequence of the favorable polarity of the σ^*(Si−C) orbital. Nevertheless, the $\sigma(\text{Si−C})\rightarrow\sigma^*(\text{C−H})$ interaction is instrumental in removing excess negative charge from the Si atom. Because of the T_d symmetry of the molecule there are 24 $\sigma\rightarrow\sigma^*$ interactions, i.e., six interactions per Si−C bond. The resulting delocalization builds some π-bond character into the Si−C bonds, making them slightly shorter and stronger than one would expect for purely single bonds. On the other hand, population of the σ^*(Si−C) orbitals is expected to make the Si−C bonds longer and weaker. Here the empty $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals of silicon play an important role.[36] Partially superimposed upon the σ^*(Si−C) orbitals, they enhance the acceptor function of the Si atom and the π-bond character of the Si−C bonds without increasing the antibonding character of the $\sigma(\text{C−H})\rightarrow\sigma^*(\text{Si−C})$ delocalization. Indeed, the length of the Si−C bond in tetramethylsilane increases by 0.015 Å in going from the fully staggered to the fully eclipsed conformation of the molecule, according to our MO calculations at the HF/6-31G*, MP2(fc)/6-31G*, and B3LYP/6-31G* levels.[5]

In tetraphenylsilane, the equilibrium conformation of the molecule (see Figure 1) is such that the π-system on one side of ring A is in close proximity of the largest lobe of the polar σ^*(Si−C1D) orbital. The torsion angle C6A−C1A−Si−C1D, about −80°, favors a strong interaction. On the other side of ring A, the π-system interacts less strongly with the σ^*(Si−C1B) orbital (the torsion angle C6A−C1A−Si−C1B is close to 40°). No appreciable interaction occurs with the σ^*(Si−C1C) orbital, because the torsion angle C6A−C1A−Si−C1C is about 160°. Rings B, C, and D behave in the same way, due to the symmetry of the molecule. Natural bond orbital analysis[35] shows that the $\pi\rightarrow\sigma^*$ delocalization, or negative hyperconjugation,[37] is quite pronounced in tetraphenylsilane. It has, again, a complex effect on the Si−C bonds, which are made shorter and stronger by the enhanced π-bond character, while tending to become longer and weaker because of the population of the σ^*(Si−C) orbitals. Delocalization of the ring π orbitals into the empty 3d orbitals of silicon is again possible. However, the absence of hydrogen atoms on C1A precludes the $\sigma(\text{Si−C})\rightarrow\sigma^*(\text{C−H})$ delocalization that occurs in tetramethylsilane. Thus, the increased electron density at Si is not relieved, causing the covalent radius of Si to increase slightly. This apparently compensates for the shorter covalent radius of C(sp^2) vs C(sp^3), making the lengths of the Si−Ph and Si−Me bonds about the same.

X-ray photoelectron spectra give a clear indication that $\pi\rightarrow\sigma^*$ delocalization is important in tetraphenylsilane. The ionization energies of the core electrons are a measure of the ability of a molecule to accept positive or negative charge at specific sites and are thus directly related to electronegativities and bond strengths. The binding energy of the Si($2p_{3/2}$) core electrons of tetramethylsilane is 105.82−106.04 eV from accurate gas-phase studies.[38−45] The corresponding binding energy for tetraphenylsilane is 100.5−102.4 eV, from less accurate solid-state studies.[43,46] The difference is consistent with a building up of negative charge on the Si atom of tetraphenylsilane as compared with tetramethylsilane.[47] If the four methyl groups are replaced by fluorines, the Si($2p_{3/2}$) binding energy increases to 111.46−111.70 eV,[38,39,42−44,48] due to withdrawal of negative charge from the central atom by the strongly electronegative substituents. Evidence for π-delocalization across the Si−Ph bond in Ph_3SiX compounds has recently been obtained by comparing the Si(1s) and Si(2p) core excitation spectra of various Ph_3SiX and Me_3SiX species.[49]

Valence band photoelectron spectra from gas-phase studies also point to $\pi \rightarrow \sigma^*$ delocalization in tetraphenylsilane. The peak at lowest ionization potential of tetramethylsilane, 10.35−10.45 eV,[50−52] is assigned to a triply degenerate silicon−carbon bonding orbital, $3t_2$, composed mainly of C(2p) and Si(3p) atomic orbitals. The corresponding orbital of tetraphenylsilane appears as a well-resolved peak at 10.17 eV.[53] The difference in ionization potential is consistent with a slightly less polar Si−C bond in tetraphenylsilane as compared with tetramethylsilane. Replacing the four methyl groups with fluorines raises the ionization potential of $3t_2$ to 17.4 eV,[50] due to the high polarity of the Si−F bonds.

Additional evidence for a build up of negative charge on the central atom of tetraphenylsilane, as compared with tetramethylsilane, comes from NMR spectroscopy measurements. The ^{29}Si NMR signal of tetraphenylsilane is shifted upfield by 13.98 ppm with respect to the corresponding signal of tetramethylsilane; this shielding has been explained by a $\pi \rightarrow \sigma^*$ charge transfer.[54]

The importance of negative hyperconjugation in stabilizing organosilicon compounds is also seen in the molecular structures of phenyltrimethylsilane, Me_3Si-Ph,[2] and vinyltrimethylsilane, $Me_3Si-CH{=}CH_2$.[55] These molecules have a minimum energy conformation in which one of the methyl groups eclipses the benzene ring or the C═C bond, thus favoring $\pi \rightarrow \sigma^*$(Si−C) and $\pi \rightarrow$3d(Si) interactions on both sides of the phenyl or vinyl plane.

The length of the Si−C bond in crystalline tetraphenylsilane has been determined repeatedly by room-temperature X-ray crystallography.[9−12] The majority of these studies, however, are of rather poor quality by today's standards. The most accurate study is that by Gruhnert et al.,[12] who used only high-order data ($\sin\theta/\lambda > 0.48$ Å^{-1}) in their refinement. This procedure reduces the asphericity shifts caused by the nonspherical distribution of valence electrons and makes the X-ray diffraction bond distance reasonably close to the distance between average nuclear positions, r_α. The length of the Si−C bond obtained by Gruhnert et al.,[12] 1.878(2) Å, compares well with the r_g value from the present study, 1.881 ± 0.004 Å. The distance in r_α representation is supposed to be slightly shorter than that in r_g.[56]

The Bond Angles at Silicon. The MO calculations indicate that the angle C1A−Si−C1B is one to two degrees smaller than ∠C1A−Si−C1C, see Table 1, in agreement with our MM3 calculations, ∠C1A−Si−C1B = 108.5° and ∠C1A−Si−C1C = 110.0°, and earlier MM2 calculations.[57] The difference being so small hinders the determination of these angles by electron diffraction alone. This is why now we ignore the findings of the previous analysis[6] with regard to these angles (Table 5), but find comforting that the X-ray diffraction study by Gruhnert et al.[12] yields ∠C1A−Si−C1B = 108.3(1)° and ∠C1A−Si−C1C = 110.0(1)°.

Comparison with the other tetraphenyl derivatives of group IV elements, MPh_4, all having S_4 crystallographic symmetry in the solid state, indicates a regular variation of the distorted tetrahedral angles at M.[10,54] The C1A−M−C1B angle increases gradually with r(M−C); it equals the regular tetrahedral angle (and hence ∠C1A−M−C1C) when r(M−C) = 2.0 Å. Thus, the tetrahedral core of these molecules is slightly elongated along the S_4 axis when M = C, Si, Ge, and slightly compressed when M = Sn, Pb. This has been attributed to an interplay of repulsive and attractive interactions between adjacent phenyl groups, subject to the length of the M−C bond.[54]

The Benzene Ring. The mean length of the ring C−C bonds in tetraphenylsilane, $\langle r_g(C-C)\rangle = 1.401 \pm 0.003$ Å, is accurately determined from electron diffraction and is virtually the same as in phenylsilane, 1.403 ± 0.003 Å,[24] and phenyltrimethylsilane, 1.402 ± 0.003 Å.[2] The deformation of the benzene ring caused by silicon substitution emerges from the MO calculations, see Tables 1 and 5. The calculated ring angles agree with those reported by Gruhnert et al.[12] for crystalline tetraphenylsilane, $\alpha = 117.6(2)°$ and $\beta = 121.3-121.4(3)°$. These geometrical changes are similar to those reported for free phenylsilane[24] and phenyltrimethylsilane.[2]

At variance with many other benzene derivatives studied in our laboratories, the present molecule has proved unamenable to an accurate determination of the ring angle α from electron diffraction. This appears to be a consequence of the high-amplitude bending motions of the phenyl groups. Ignoring these motions leads to an unacceptably high value of α. On the other hand, simultaneously refining the angle α and the bending parameter θ has proved unfeasible, due to high correlation between these parameters. We have found that the experimental data could be approximated equally well by assuming different values for the angle α, and allowing θ to refine. In view of the evidence for a pronounced bending motion of the phenyl groups provided by our spectroscopic calculations, we have eventually assumed the angle α at its calculated (B3LYP) value. This leads to a value of θ of 8.4 ± 0.8°, consistent with the large-amplitude motion of the phenyl groups.

Conclusions

We draw the following conclusions.

(1) The twist angle of the phenyl group in free tetraphenylsilane of S_4 symmetry is $\tau = 40 \pm 2°$ from gas-phase electron diffraction, in agreement with MO results and earlier empirical calculations.[7,8]

(2) The length of the Si−C bond in tetraphenylsilane is $r_g = 1.881 \pm 0.004$ Å from gas-phase electron diffraction. The length of the corresponding bond in tetramethylsilane is $r_g = 1.877 \pm 0.004$ Å from electron diffraction data taken with the same apparatus.[5] A nearly equal length of the Si−C bond in the two molecules is also indicated by ab initio/DFT calculations. This cannot be attributed to steric hindrance in tetraphenylsilane; rather, it is due to a delicate balance of subtle stereoelectronic effects, involving electron delocalization into σ^*(Si−C) and 3d(Si) orbitals. Evidence for $\pi \rightarrow \sigma^*$ delocalization in tetraphenylsilane comes from X-ray and valence band photoelectron spectroscopy and ^{29}Si NMR spectroscopy.

(3) The ipso ring angle of the phenyl group is 117.5° from the B3LYP calculations, in agreement with solid-state results. The effect of the crystal environment on the molecular structure of tetraphenylsilane appears to consist merely of an increase of the twist angle τ by about 12°, with no measurable change in the other geometrical parameters.

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Supporting Information Available: Table 1S giving the total experimental electron diffraction intensities of tetraphenylsilane for two camera distances (four pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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