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Molecular structure of phenylsilane: a study by gas-phase electron diffraction and ab initio molecular orbital calculations

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Abstract

The molecular structure of phenylsilane has been determined accurately by gas-phase electron diffraction and ab initio MO calculations at the MP2(f.c.)/6-31G* level. The calculations indicate that the perpendicular conformation of the molecule, with a Si–H bond in a plane orthogonal to the plane of the benzene ring, is the potential energy minimum. The coplanar conformation, with a Si–H bond in the plane of the ring, corresponds to a rotational transition state. However, the difference in energy is very small, 0.13 kJ mol^{-1}, implying free rotation of the substituent at the temperature of the electron diffraction experiment (301 K). Important bond lengths from electron diffraction are: $<r_g(\text{C–C})> = 1.403 \pm 0.003$ Å, $r_g(\text{Si–C}) = 1.870 \pm 0.004$ Å, and $r_g(\text{Si–H}) = 1.497 \pm 0.007$ Å. The calculations indicate that the C_{ipso}–C_{ortho} bonds are 0.010 Å longer than the other C–C bonds. The internal ring angle at the *ipso* position is 118.1 ± 0.2° from electron diffraction and 118.0° from calculations. This confirms the more than 40-year old suggestion of a possible angular deformation of the ring in phenylsilane, in an early electron diffraction study by F.A. Keidel, S.H. Bauer, J. Chem. Phys. 25 (1956) 1218. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Phenylsilane; Molecular structure; Gas-phase electron diffraction; Ab initio MO calculations

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1. Introduction

Possible deformation of the benzene ring caused by substitution was first suggested by Keidel and Bauer in an early (1956) electron diffraction study of the molecular structure of phenylsilane, C_6H_5–SiH_3 [1]. Although their analysis of the experimental data was not based on the least-squares method, these authors found that the positions of two Si···C peaks in the experimental radial distribution could be better reproduced by a model where the internal ring angles α and δ (see Fig. 1) were 117.4 and 120.8°, respectively, rather than 120°.

Nowadays, accurately determining the molecular structure of a benzene derivative is a powerful tool for investigating the nature of the ring-substituent interaction [2,3]. In monosubstituted derivatives the ring symmetry is generally lowered from D_{6h} to C_{2v}; the most affected geometrical parameter is the angle α, which varies with the electronegativity of the substituent from 112° (C_6H_5Li) to 126° ($C_6H_5N_2^+$). Also affected—but to a lesser extent—are the other ring angles and the *a* bond distances.

As a part of our gas-phase studies on monosubstituted benzene derivatives [4–7] and a contribution to the study of the Si–C bond in free molecules [7–11] we have performed a new electron diffraction investigation of phenylsilane. We have also run ab initio molecular orbital (MO) calculations on phenylsilane at the MP2 level of theory. Apart from giving information on the conformational properties of the silyl group and their effect on the geometry of the molecule, the calculations provide reliable values for the differences between the lengths of the ring C–C bonds, which cannot be determined from electron diffraction alone. The structure and conformation of phenylsilane have already been

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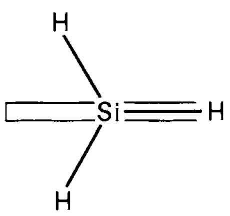
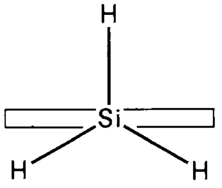


(1a)



(1b)

investigated by ab initio MO calculations at the HF level [12,13].

2. Theoretical calculations

Ab initio MO calculations were carried out at the second order of the Møller–Plesset perturbation theory [14] (MP2, frozen-core approximation) with the 6-31G* basis set [15] and gradient optimization [16], using the Gaussian 94 package [17]. Two models were considered for phenylsilane, one with a Si–H bond in the plane of the benzene ring (**1a**, coplanar conformation), the other with a Si–H bond in a plane orthogonal to the ring plane (**1b**, perpendicular conformation). The symmetry C_s was assumed for both models. The benzene ring was not subjected to the planarity constraint in **1b**. The molecular geometry of phenylsilane from the MP2 calculations is compared in Table 1 with that obtained at the HF level using the same basis set [12].

Molecular mechanics calculations were carried out with the MM3 force field [18], using the 1992 version of the program. They provided vibrational amplitudes utilized in the electron diffraction least-squares refinement and energy differences between conformers.

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

3. Electron diffraction

3.1. Experiment

The purity of the phenylsilane sample (Fluka) used in the electron diffraction experiment was 99% as checked by gas chromatography. The main impurity was identified as cyclohexylsilane by mass spectrometry. The electron diffraction photographs were taken with the

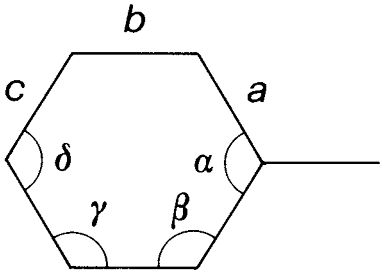


Fig. 1. Lettering of bond distances and angles in a monosubstituted benzene ring of C_{2v} symmetry.

Table 1
Molecular geometry of the coplanar (**1a**) and perpendicular (**1b**) conformations of phenylsilane from ab initio MO calculations

Parameter	HF/6-31G*[a]		MP2(f.c.)/6-31G*	
	1a	**1b**	**1a**	**1b**
Bond distances (Å)				
r(C1–C2)	1.3941	1.3956	1.4057	1.4064
r(C1–C6)	1.3973	1.3956	1.4072	1.4064
r(C2–C3)	1.3873	1.3853	1.3972	1.3961
r(C5–C6)	1.3833	1.3853	1.3952	1.3961
r(C3–C4)	1.3836	1.3855	1.3954	1.3963
r(C4–C5)	1.3873	1.3855	1.3973	1.3963
r(C2–H2)	1.0762	1.0767	1.0887	1.0892
r(C6–H6)	1.0772	1.0767	1.0896	1.0892
r(C3–H3)	1.0756	1.0756	1.0877	1.0876
r(C5–H5)	1.0756	1.0756	1.0877	1.0876
r(C4–H4)	1.0756	1.0756	1.0875	1.0875
r(Si7–C1)	1.8819	1.8818	1.8788	1.8782
r(Si7–H71)	1.4762	1.4783	1.4859	1.4881
r(Si7–H72)	1.4777	1.4767	1.4873	1.4864
Angles[b] (°)				
∠C2–C1–C6	117.84	117.86	117.99	118.01
∠C1–C2–C3	121.20	121.21	121.10	121.09
∠C1–C6–C5	121.24	121.21	121.12	121.09
∠C2–C3–C4	119.95	119.94	120.01	120.00
∠C4–C5–C6	119.93	119.94	120.00	120.00
∠C3–C4–C5	119.83	119.84	119.79	119.80
∠Si7–C1–C2	121.04	121.07	120.81	120.99
∠Si7–C1–C6	121.11	121.07	121.20	120.99
∠C1–C2–H2	119.93	119.95	119.87	119.94
∠C1–C6–H6	119.99	119.95	120.04	119.94
∠C3–C2–H2	118.87	118.84	119.03	118.96
∠C5–C6–H6	118.77	118.84	118.84	118.96
∠C1–Si7–H71	109.07	111.76	108.65	111.67
∠C1–Si7–H72	111.14	109.79	111.08	109.55
∠H71–Si7–H72	108.91	107.99	109.07	108.18
∠H72–Si7–H73	107.61	109.46	107.83	109.67
Torsion angles (°)				
C2–C1–Si7–H71	0.0[c]	−89.6	0.0[c]	−89.3
C2–C1–Si7–H72	−120.1	150.6	−120.0	150.8
C2–C1–Si7–H73	120.1	30.2	120.0	30.5
Displacements (Å) from the least-squares plane through the C atoms of the benzene ring				
C1	—	0.0022	—	0.0017
C2	—	−0.0014	—	−0.0010
C3	—	−0.0003	—	−0.0005
C4	—	0.0011	—	0.0012
Si7	—	0.0317	—	0.0447
H2	—	−0.0095	—	−0.0120
H3	—	−0.0038	—	−0.0052
H4	—	−0.0004	—	−0.0010
H71	—	1.4131	—	1.4398
H72	—	−0.6510	—	−0.6405

[a] Ref. [12].

[b] The C–C–H angles of the phenyl group involving H3, H4, and H5 are not shown; they differ from 120° by less than 0.15°.

[c] Assumed.

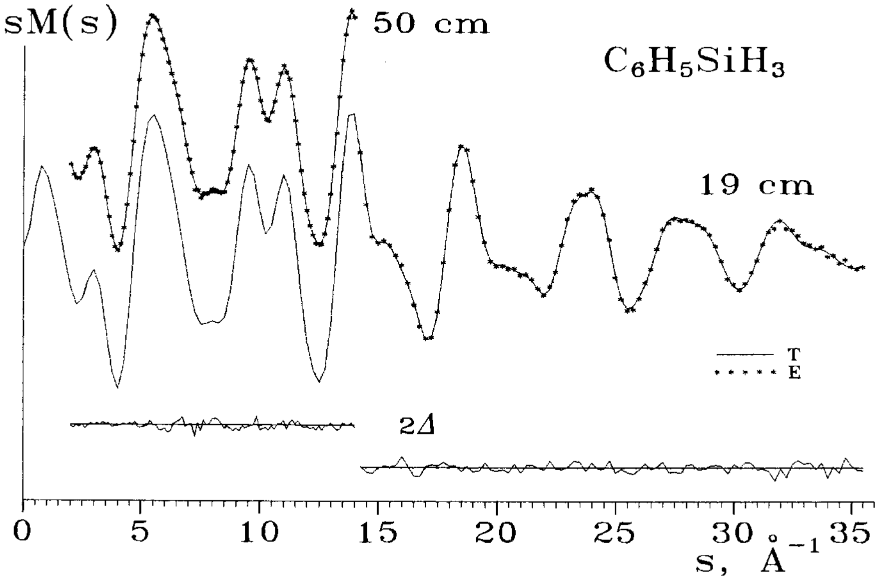


Fig. 2. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (experimental − theoretical).

Budapest EG-100A apparatus [19], using a so-called membrane nozzle [20] at a temperature of about 301 K. The electron wavelength, 0.049487 Å, was calibrated with a TlCl powder pattern ($a = 3.84145$ Å [21]). Nozzle-to-plate distances of about 50 and 19 cm were used; five and seven plates, respectively, were selected for analysis. The tracing and data reduction were carried out according to our usual procedures [22,23]; the ranges of the intensity data were $2.000 \leq s \leq 14.000$ Å^{-1} and $14.25 \leq s \leq 35.50$ Å^{-1}, with data intervals of 0.125 and 0.25 Å^{-1}, respectively. The portion of the 19 cm data set with $s < 14.25$ Å^{-1} was discarded due to high noise level.

The total experimental intensities are available from the authors upon request. The experimental molecular intensities and radial distributions are compared with those from the final refinement in Figs. 2 and 3, respectively.

3.2. Analysis

The least-squares method was applied to molecular intensities as in Refs. [22] and [23], using the same scattering functions, phase shifts, and computer programs as in Ref. [7].

The benzene ring was assumed to have C_{2v} symmetry and the silyl group C_{3v} symmetry. The C–H bonds were represented by a mean bond length and each was assumed to bisect the corresponding C–C–C angle, as in our previous studies of monosubstituted benzene derivatives [4–7]. Under these constraints the geometry of the molecule is described by ten independent parameters, which were chosen as follows (see Fig. 4 for the numbering of atoms and Fig. 1 for the lettering of bond distances and angles of a benzene ring of C_{2v} symmetry): (i) four bond distances, $r(\text{C1–C2}) = a$, r(Si7–C1), $<r(\text{C–H})>$, and r(Si7–H71); (ii) two differences between bond distances, $\Delta_1(\text{C–C}) = r(\text{C1–C2}) - r(\text{C2–C3}) = a - b$ and $\Delta_2(\text{C–C}) = r(\text{C2–C3}) - r(\text{C3–C4}) = b - c$; (iii) three bond angles, $\angle\text{C2–C1–C6} = \alpha$, $\angle\text{C1–C2–C3} = \beta$, and $\angle$C1–Si7–H71; (iv) the angle of torsion of the silyl group, $\tau = $ C2–C1–Si7–H71.

The three different bond distances and four different angles of the benzene ring (Fig. 1) are linked by two equations of geometrical constraint, expressing the conditions of planarity and ring closure [24]. 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 MP2 calculations, as was the angle C1–Si7–H71. The angle β was assumed to be linearly related to α, according to the relationship $\Delta\beta = -0.6052\Delta\alpha - 0.084°$ (where $\Delta\alpha$ and $\Delta\beta$ are deviations from 120°). This relationship has been recently obtained by regression from the ab initio MO geometries of 22 monosubstituted benzene rings [25], and appears to be more accurate than the previously used relationship from X-ray diffraction geometries [24]—at least for those derivatives where mesomeric interactions between the ring and the substituent do not occur.

Eleven mean amplitudes of vibration, l, were also treated as independent variables. They were coupled in groups to other amplitudes with constrained differ-

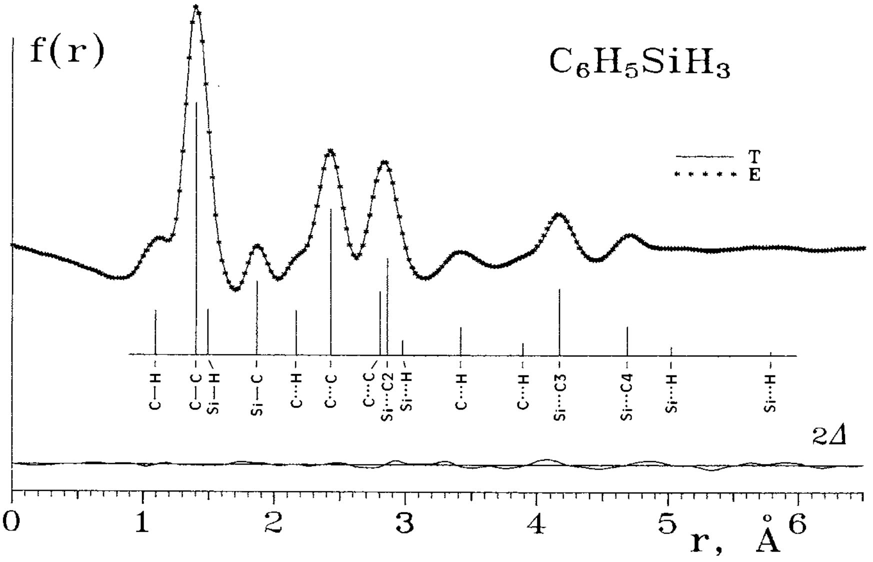


Fig. 3. Radial distribution curves (E, experimental; T, theoretical). They were calculated using an artificial damping factor exp($-0.002s^2$); theoretical values were used in the $0.00 \leq s \leq 1.75$ Å^{-1} region. The positions of the most important distances are marked with vertical bars, the heights of which are proportional to the relative weights of the distances. Also shown is the difference curve (experimental – theoretical).

ences, Δl. These differences and other assumed amplitudes were taken from spectroscopic calculations based on the MM3 force field [18]. The effect of reasonably different choices of the Δl values on the geometrical parameters was found to be marginal.

In the course of the analysis it became clear that the electron diffraction intensities are fitted equally well by models having any value of the angle of torsion of the silyl group, τ. This finding is consistent with the very low value of the torsional barrier, $V_6 = 0.074$ kJ mol^{-1} from a study of phenylsilane by microwave spectroscopy [26]. The angle τ was therefore given the effective value of 15°, corresponding to free rotation of the substituent about the Si–C bond.

Important molecular parameters from the final refinement are presented in Table 2, showing also the coupling of vibrational amplitudes. Correlation matrix elements greater than 0.5 are shown in Table 3. We point out that the least-squares standard deviations in Table 2 should be considered merely as indicators of precision; they are sometimes unrealistically small due to the constraints employed in the refinement.

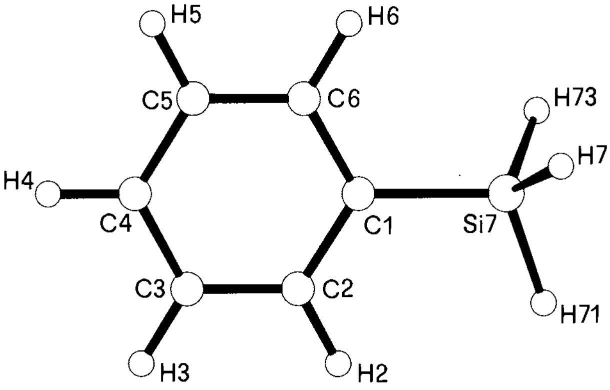


Fig. 4. Numbering of atoms in phenylsilane.

4. Results and discussion

Before discussing our present results in detail we wish to pay tribute to Keidel and Bauer's early study [1] in which they communicated the overall structure of phenylsilane and pioneered the notion of benzene ring deformation under substituent impact.

The molecular structure of gaseous phenysilane from our electron diffraction study is compared with the structure obtained by ab initio MO calculations in Table 4.

4.1. *Molecular conformation*

The MP2 calculations confirm that the perpendicular conformer (**1b**) is slightly lower in energy than the coplanar conformer (**1a**), as indicated by previous MO studies at the HF level [12,13]. The same indication is given by molecular mechanics (MM3) calculations. Frequency calculations show that **1b** corresponds to a local minimum while **1a** is a rotational transition state. The energy difference between **1a** and **1b** is small at all levels of calculation [HF/4-21G(C,H), 3-21G(Si), 0.01 kJ mol^{-1} [13]; HF/6-31G*, 0.07 kJ mol^{-1} [12]; MP2(f.c.)/6-31G*, 0.13 kJ mol^{-1}; the value from molecular mechanics is 0.03 kJ mol^{-1}]. It compares well with the 6-fold barrier to internal rotation of the silyl group, $V_6 = 0.074$ kJ mol^{-1} from microwave spectroscopy [26].

With such a small barrier the silyl group of gaseous phenylsilane is freely rotating at r.t., as witnessed by the

Table 2
Molecular parameters of phenylsilane from electron diffraction[a].
Distances and mean amplitudes of vibration[b]

Atom pair	Multiplicity	r_a (Å)	l (Å)		Coupling scheme[d]
			Exp.	Calc.[c]	
C1–C2	2	1.4087(2)	0.0503(6)	0.045	i
C2–C3	2	1.3984(2)[e]	0.0503	0.045	i
C3–C4	2	1.3986(2)[e]	0.0503	0.045	i
Si7–C1	1	1.8684(11)	0.053(1)	0.052	ii
<C–H>	5	1.095(2)	0.077(3)	0.077	iii
Si7–H71	3	1.492(4)	0.090[f]	0.090	
C1···C3	2	2.444(1)[e]	0.0619(7)	0.057	iv
C1···C4	1	2.822(3)[e]	0.066(1)	0.063	v
C2···C4	2	2.421(1)[e]	0.0619	0.057	iv
C2···C5	2	2.794(2)[e]	0.066	0.063	v
C2···C6	1	2.416(2)[e]	0.0619	0.057	iv
C3···C5	1	2.422(1)[e]	0.0619	0.057	iv
Si7···C2	2	2.860(1)[e]	0.080	0.077	v
Si7···C3	2	4.171(1)[e]	0.079(2)	0.073	vi
Si7···C4	1	4.691(2)[e]	0.076(4)	0.069	vii
C1···H2	2	2.168(2)[e]	0.093(3)	0.099	viii
C1···H3	2	3.433(2)[e]	0.096(4)	0.096	ix
C1···H4	1	3.917(3)[e]	0.095(9)	0.095	x
C2···H3	2	2.165(2)[e]	0.093	0.099	viii
C2···H4	2	3.414(2)[e]	0.096	0.096	ix
C2···H6	2	3.889(2)[e]	0.095	0.095	x
C2···H5	2	3.412(3)[e]	0.096	0.096	ix
C3···H2	2	2.159(2)[e]	0.093	0.099	viii
C3···H4	2	2.165(2)[e]	0.093	0.099	viii
C3···H5	2	3.415(2)[e]	0.096	0.096	ix
C3···H6	2	3.889(2)[e]	0.095	0.095	x
C4···H2	2	3.410(2)[e]	0.096	0.096	ix
C4···H3	2	2.165(2)[e]	0.093	0.099	viii
Si7···H2	2	2.980(1)[e]	0.166(13)	0.151	xi
Si7···H3	2	5.025(2)[e]	0.135	0.120	xi
Si7···H4	1	5.786(3)[e]	0.115	0.100	xi
C1···H71	3	2.766(4)[e]	0.131	0.128	v
C4···H71	3	5.393(3)[e]	0.168[f]	0.168	
Angles (°)					
∠C2–C1–C6 (α)	118.11(16)				
∠C1–C2–C3 (β)	121.06(10)[e]				
∠C2–C3–C4 (γ)	119.90(3)[e]				
∠C3–C4–C5 (δ)	119.97(10)[e]				
∠C1–Si7–H71	110.3[g]				
τ[h]	15.0[i]				
Differences between bond distances (Å)					
Δ_1(C–C)[j]	0.0103[g]				
Δ_2(C–C)[k]	−0.0002[g]				

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[a] Least-squares standard deviations are given in parentheses in units of the last digit.

[b] To economize on space, the table does not include H···H pairs and those C···H pairs whose lengths depend on the conformation of the molecule.

[c] From molecular mechanics 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 molecular mechanics calculations.

[g] Assumed from ab initio MO calculations [MP2(f.c.)/6-31G* level].

[h] Angle of torsion of the SiH_3 group, C2–C1–Si7–H71.

[i] Assumed.

[j] $\Delta_1(\mathrm{C-C}) = r(\mathrm{C1-C2}) - r(\mathrm{C2-C3})$.

[k] $\Delta_2(\mathrm{C-C}) = r(\mathrm{C2-C3}) - r(\mathrm{C3-C4})$.

Table 3
Correlation matrix elements with absolute values >0.5

I	*j*	x_{ij} $(i \neq j)$
r(Si–C)	α	0.52
r(Si–H)	S^{a}_{50}	0.59
l(C–C)	l(C–H)	0.57
l(C–C)	l(C1···C3)	0.59
l(C–C)	S^{b}_{19}	0.89
l(C–H)	S^{b}_{19}	0.67
l(C1···C3)	S^{b}_{19}	0.66

[a] Scale factor for the 50 cm data set.
[b] Scale factor for the 19 cm data set.

rotational fine structure which appears on certain bands arising from vibrations of the silyl group in the gas-phase IR spectrum [28,29].

Due to the small energy difference between **1a** and **1b**, intermolecular interactions in a condensed phase may well destabilize **1b** with respect to **1a**. It is not surprising, therefore, that the coplanar conformer **1a** was found to be more stable than **1b** in a proton magnetic resonance study of phenylsilane oriented in a nematic mesophase [30].

4.2. Geometry of the silyl group

The length of the Si–C bond in phenylsilane is determined accurately from electron diffraction, since the corresponding peak of the radial distribution (Fig. 3) does not include contributions from other atomic pairs. The value obtained, $r_g = 1.870 \pm 0.004$ Å[1], agrees with those for triphenylsilane, $r_g = 1.872 \pm 0.004$ Å [8], and tetraphenylsilane, $r_g = 1.871 \pm 0.004$ Å [9]. Values of r(Si–C) in the range 1.872–1.878 Å have been obtained by X-ray crystallography for 1,8-disilylnaphthalene [31], 1,4-dibromo-2,5-disilylbenzene [32], and 9,10-disilylanthracene [33].

Table 4
Molecular geometry[a] of phenylsilane: comparison of experimental and theoretical results

Parameter[b]	Electron diffraction[c]	Ab initio MO calculations [MP2(f.c.)/6-31G* level][d,e]
a	1.410 ± 0.003	1.406
b	1.400[f]	1.396
c	1.400[f]	1.396
α	118.1 ± 0.2	118.0
β	121.1 ± 0.1	121.1
γ	119.9 ± 0.2	120.0
δ	120.0 ± 0.3	119.8
r(Si–C)	1.870 ± 0.004	1.879
r(Si–H)	1.497 ± 0.007	1.487
$<r$(C–H)$>$	1.100 ± 0.004	1.088
∠C–Si–H	110.3[f]	110.3

[a] Bond distances are given in Å, angles in °.
[b] Bond distances and angles of the benzene ring are lettered according to Fig. 1.
[c] Bond distances are r_g values. Total errors are given as error limits, and were estimated as $\sigma_T = [2\sigma^2_{LS} + (0.002r)^2 + (\Delta/2)^2]^{1/2}$ (for bond distances) and $\sigma_T = [2\sigma^2_{LS} + (\Delta/2)^2]^{1/2}$ (for angles), where σ_{LS} is the least-squares standard deviation, and $\Delta/2$ is the effect of the constraints adopted in the refinement [27].
[d] Bond distances are r_e values.
[e] Average geometry of the coplanar and perpendicular conformations of the molecule, consistent with the symmetry constraints adopted in the electron diffraction study.
[f] The differences $a-b$ and $b-c$ and the angle ∠C–Si–H have been constrained from the ab initio MO calculations.

The length of the Si–H bond from electron diffraction, $r_g = 1.497 \pm 0.007$ Å, coincides with the more accurate result obtained for trisilylmethane, $r_g = 1.497 \pm 0.003$ Å [34]. The changes in the Si–H bond lengths and C–Si–H angles that accompany the rotation of the silyl group, as obtained from MO calculations at the HF level [12,13], are confirmed by the MP2 calculations, see Table 1. It appears that the silyl hydrogens are repelled by the π-electron system of the benzene ring when they are out of the ring plane.

4.3. Benzene ring deformation

The most pronounced effect of the substituent on the ring geometry is at the *ipso* position, as is generally the case with monosubstituted benzene rings [2,3]. The value of α from electron diffraction, 118.1 ± 0.2°, has shown little sensitivity to changes in the background lines and refinement conditions and should thus be considered as accurately determined. The ring angles from theory and experiment are in excellent agreement: the values from electron diffraction are within 0.2° of the MP2 values (Table 4), which supports the accuracy of the results. The MO calculations also show that changing the conformation of the molecule from **1a** to **1b** has no effect on the ring angles, see Table 1. The more than 40-year old suggestion by Keidel and Bauer [1] of a possible angular deformation of the ring in phenylsilane is hence confirmed.

The *ipso* angle in phenylsilane is about 1° larger than the corresponding angle in trimethylsilylbenzene, $\alpha = 117.2 \pm 0.2°$ [7]. The same is true of toluene, $\alpha = 118.7 \pm 0.4°$ [22], versus *tert*-butylbenzene, $\alpha = 117.1 \pm 0.3°$ [5]. These variations of the *ipso* angle may be taken as an indication of the $-CH_3$ and $-SiH_3$ substituents becoming more electron-releasing when their hydrogen atoms are replaced by methyl groups.

The small changes in the lengths of the ring C–C bonds caused by the silyl group cannot be determined accurately by electron diffraction. The MO calculations, however, indicate that the a bonds are 0.010 Å longer than the b and c bonds (see Table 1). The difference

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[1] Here and throughout this paper total errors are given as error limits. Least-squares standard deviations are in parentheses in units of the last digit.

appears to be reliable, as it does not depend on the level of calculation. The lengthening of the *a* bonds causes the mean length of the ring C–C bonds, $< r_g(\mathrm{C{-}C}) > = 1.403 \pm 0.003$ Å, to exceed slightly the C–C bond length in unsubstituted benzene, $r_g = 1.399 \pm 0.003$ Å [35]. Unlike the individual C–C bond lengths, $< r_g(\mathrm{C{-}C}) >$ is well determined by electron diffraction and is the same as in triphenylsilane [8] and tetraphenylsilane [9].

The asymmetric attachment of the silyl group to the benzene ring in the coplanar conformation of the molecule, **1a**, is expected to cause the carbon skeleton to deviate slightly from axial symmetry [5,7,36]. While bond angles are apparently unaffected, small systematic differences between C–C bond lengths related by the C1···C4 axis are seen in Table 1. Note, however, that all differences are halved in going from HF to MP2 level.

A different kind of distortion may occur in the perpendicular conformation of the molecule, where the benzene ring was not subjected to the planarity constraint. HF/6-31G and 6-31G* MO calculations carried out on the perpendicular conformers of toluene, ethylbenzene, styrene, nitrosobenzene, benzaldehyde, and phenol, as well as on the pyramidal conformer of aniline, indicate that the ring adopts a very shallow boat-type conformation, with deviations from planarity not exceeding a few thousandths of an ångström [37]. The substituent atom linked to the ring is, in general, more displaced than the ring carbons, up to about 0.05 Å in some of these molecules. The decrease in total energy occurring upon relaxation of the planarity constraint is calculated to be 0.03–0.37 kJ mol^{-1} [37], implying that the driving force for departure from coplanarity is weak. The HF/6-31G* calculations for the perpendicular conformer of phenylsilane indicate a similar distortion [12]. Correction for electron correlation at the MP2 level confirms the minute deviations from planarity of the ring carbons, while the deviations of silicon and the ring hydrogens increase appreciably, see Table 1. This is at variance with aniline, where correction for electron correlation at the MP2 level gives rise to a substantial change in the pattern of small deviations from planarity [6].

With regard to C–H bonds, HF and MP2 calculations show that in both **1a** and **1b** the two bonds at the *ortho* positions, C2–H2 and C6–H6, are 0.01–0.02 Å longer than the others. They are also bent away from the substituent by about 1°, see Table 1. As with *tert*-butylbenzene [5] and trimethylsilylbenzene [7], such effects are likely to originate from non-bonded interactions with the substituent.

5. Supplementary material available

A listing of total experimental electron diffraction intensities of phenylsilane for two camera distances (four pages) is available from the authors upon request.

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