Molecular structure and conformation of trimethylsilylbenzene: a study by gas-phase electron diffraction and theoretical calculations [1]

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Abstract

The molecular structure and conformation of trimethylsilylbenzene have been investigated by gas-phase electron diffraction, molecular mechanics (MM3 force field), and ab initio MO calculations at the HF/6-31G* and MP2(f.c.)/6-31G* levels. The theoretical calculations show that the coplanar conformation of the molecule, with an Si–Me bond in the plane of the benzene ring, is a potential energy minimum. The perpendicular conformation, with an Si–Me bond in a plane orthogonal to the ring plane, is 0.2–0.5 kJ mol^{-1} higher in energy and corresponds to a rotational transition state. This low barrier makes the conformational space of the molecule almost evenly populated at the temperature of the electron diffraction experiment (305 K). A model approximating a freely rotating SiMe$_3$ group is consistent with the experimental data. Important geometrical parameters from electron diffraction are $\langle r_g(\text{C–C}) \rangle = 1.402 \pm 0.003$ Å, $\langle r_g(\text{Si–C}) \rangle = 1.880 \pm 0.004$ Å, and $\angle C_{\text{ortho}}-C_{\text{ipso}}-C_{\text{ortho}} = 117.2 \pm 0.2°$. The corresponding r_e values from MP2 calculations are 1.400 Å, 1.887 Å, and 117.4°. The MO calculations also show that the $C_{\text{ipso}}-C_{\text{ortho}}$ bonds are 0.011 Å longer than the other C–C bonds. The MM3 and MO calculations indicate that the lengths of the Si–Me and Si–Ph bonds differ by only a few thousandths of an ångström. This is less than what chemical expectation would suggest, but is in agreement with electron diffraction results from molecules containing either Si–Me or Si–Ph bonds. © 1997 Elsevier Science S.A.

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

1. Introduction

The accurate determination of structural substituent effects in benzene derivatives is an important tool for investigating the interactions between the benzene ring and its substituents [1,2]. The trimethylsilyl group is expected to cause considerable deformation of the benzene ring. In fact, possible ring distortion was first noted in an early electron diffraction study of phenylsilane [3]. As part of our studies on the gas-phase structure of monosubstituted benzene derivatives [4] we have

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recently determined the molecular structure of *tert*-butylbenzene, C$_6$H$_5$–CMe$_3$, from electron diffraction, molecular mechanics (MM), and ab initio molecular orbital (MO) calculations [5]. We now report the structure of the silicon analogue, trimethylsilylbenzene (C$_6$H$_5$–SiMe$_3$), also as a contribution to the study of the Si–C bond in free molecules [6–11].

A point of particular interest is the conformation assumed by the molecule in the gaseous phase. In *tert*-butylbenzene our calculations have shown that the coplanar conformation, having one of the C–Me bonds in the plane of the ring, is the potential energy minimum, while the perpendicular conformation lies 2–3 kJ mol^{-1} higher in energy and corresponds to a transition state [5]. Also, the coplanar model fits the electron diffraction intensities better than the perpendicular model. The conformational preferences of trimethylsilylbenzene are expected to be less pronounced than those of its carbon analogue, since Si–C bonds are longer and weaker than C–C bonds.

A preliminary account of some of the results from the present study has appeared [12].

2. Theoretical calculations

Two models were considered for trimethylsilylbenzene, one with an Si–Me bond in the plane of the benzene ring (**1a**, coplanar conformation), the other with an Si–Me bond in a plane orthogonal to the ring plane (**1b**, perpendicular conformation). The symmetry C_s was assumed for both models, the mirror plane coinciding with the ring plane in **1a** and being orthogo-

nal to it in **1b**. The benzene ring was not subjected to the planarity constraint in **1b**.
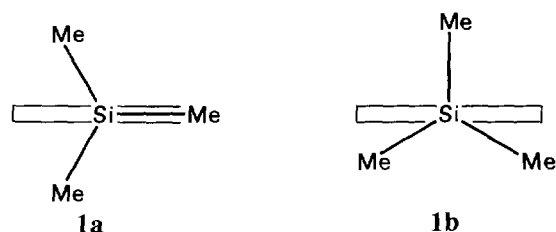
Ab initio MO calculations were carried out at the Hartree–Fock level and, in the case of **1a**, also at the

Table 1
Molecular geometry of trimethylsilylbenzene from ab initio MO calculations

Parameter	Coplanar conformation (**1a**)		Perpendicular conformation (**1b**), HF/6-31G *
	HF/6-31G *	MP2(f.c.)/6-31G *	
Bond distances (Å)			
r(C1–C2)	1.395	1.406	1.397
r(C1–C6)	1.398	1.408	1.397
r(C2–C3)	1.388	1.397	1.386
r(C5–C6)	1.384	1.395	1.386
r(C3–C4)	1.384	1.396	1.385
r(C4–C5)	1.387	1.397	1.385
r(Si7–C1)	1.896	1.888	1.897
r(Si7–C8)	1.892	1.886	1.893
r(Si7–C9)	1.893	1.887	1.893
$\langle r(C–H)_{Ph} \rangle$	1.076	1.088	1.076
$\langle r(C–H)_{Me} \rangle$	1.087	1.095	1.087
Angles (deg) [a]			
∠C2–C1–C6	117.2	117.4	117.2
∠C1–C2–C3	121.5	121.4	121.6
∠C1–C6–C5	121.6	121.5	121.6
∠C2–C3–C4	120.0	120.0	120.0
∠C4–C5–C6	119.9	119.9	120.0
∠C3–C4–C5	119.6	119.7	119.6
∠Si7–C1–C2	122.3	122.3	121.4
∠Si7–C1–C6	120.4	120.3	121.4
∠C1–Si7–C8	110.2	109.9	109.8
∠C1–Si7–C9	109.5	109.2	109.9
∠C8–Si7–C9	109.2	109.6	109.2
∠C9–Si7–C10	109.1	109.5	109.0
∠C1–C2–H2	120.0	119.8	120.0
∠C1–C6–H6	119.9	119.9	120.0
∠C3–C2–H2	118.5	118.7	118.4
∠C5–C6–H6	118.5	118.6	118.4
$< ∠Si–C–H_{Me} >$	111.4	111.2	111.4
$< ∠H–C–H_{Me} >$	107.5	107.7	107.4
Torsion angles (deg)			
C2–C1–Si7–C8	0.0 [b]	0.0 [b]	−89.4
C2–C1–Si7–C9	−120.2	−120.2	150.5
C1–Si7–C8–H81	−180.0 [b]	−180.0 [b]	−180.0 [b]
C1–Si7–C8–H82	60.7	60.6	59.9
C1–Si7–C9–H91	−179.3	−179.3	−176.9
C1–Si7–C9–H92	60.8	60.7	63.7
C1–Si7–C9–H93	−59.4	−59.3	−57.3

[a] The C–C–H angles of the phenyl group involving H3, H4, and H5 are not shown; they differ from 120° by no more than 0.2°. [b] Assumed.

second order of the Møller–Plesset perturbation theory [13] (MP2, frozen-core approximation) with the 6-31G* basis set [14] and gradient optimization [15], using the GAUSSIAN 94 package [16]. MM calculations were carried out with the MM3 force field [17], using the 1992 version of the program. All calculations were run on an Alpha AXP-3000/500 cluster at the University of Rome "La Sapienza". The molecular geometry of trimethylsilylbenzene from the MO calculations is reported in Table 1.

3. Electron diffraction

3.1. Experiment

The purity of the trimethylsilylbenzene sample (Fluka) used in the electron diffraction experiment was checked by gas chromatography, and was found to be better than 99%. The electron diffraction photographs were taken with the Budapest EG-100A apparatus [18], using a so-called membrane nozzle [19] at a temperature of about 305 K. The electron wavelength, 0.04953 Å, was calibrated with a TlCl powder pattern ($a = 3.84145$ Å [20]). Nozzle-to-plate distances of about 50 and 19 cm were used. The tracing and data reduction were carried out according to our usual procedures [21,22]; the ranges of the intensity data were $1.875 \le s \le 13.875$ Å^{-1} and $9.50 \le s \le 35.75$ Å^{-1}, with data intervals of 0.125 Å^{-1} and 0.25 Å^{-1} respectively.

The total experimental intensities are available from the authors upon request. Molecular intensities and radial distributions are presented in Figs. 1 and 2 respectively.

3.2. Analysis

The least squares method was applied to molecular intensities according to our normal procedure [21,22], using a modified version of the program by Seip and co-workers [23]. The inelastic and elastic scattering functions and the phase shifts were taken from Ref. [24] and Ref. [25] respectively.

The benzene ring was assumed to have C_{2v} symmetry and the trimethylsilyl group C_{3v} symmetry. The three methyl groups were also assumed to have C_{3v} symmetry, implying equal lengths for all C–H$_{Me}$ bonds and equal Si–C–H$_{Me}$ angles. One of the C–H bonds of each methyl group was assumed to be anti to the Si7–Cl bond, in accordance with the MO and MM calculations. The five C–H bonds of the phenyl group 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].

Under the above constraints, the geometry of the molecule is described by 12 independent parameters, which we have chosen as follows (see Fig. 3 for the numbering of atoms and Fig. 4 for the lettering of bond distances and angles of a benzene ring of C_{2v} symmetry): (i) three bond distances, $r(C1–C2) = a$, $r(Si7–C1)$, and $r(C–H)_{Ph}$; (ii) four differences between bond distances, $\Delta_1(C–C) = r(C1–C2) – r(C2–C3) = a – b$, $\Delta_2(C–C) = r(C2–C3) – r(C3–C4) = b – c$, $\Delta(Si–C) = r(Si7–C8) – r(Si7–C1)$, and $\Delta(C–H) = r(C–H)_{Me} – r(C–H)_{Ph}$; (iii) four bond angles, $\angle C2–C1–C6 = \alpha$, $\angle C1–C2–C3 = \beta$, $\angle C1–Si7–C8$, and $\angle Si–C–H_{Me}$; (iv) the angle of torsion of the SiMe$_3$ group, $\tau = C2$–C1–Si7–C8.

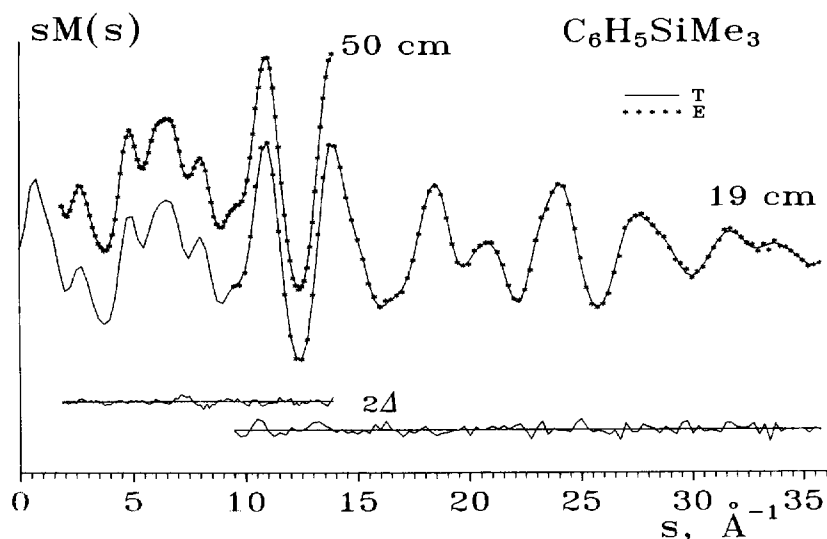Note that the three different bond distances and four

Fig. 1. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical for the model obtained from refinement C). Also shown are the difference curves (experimental − theoretical).
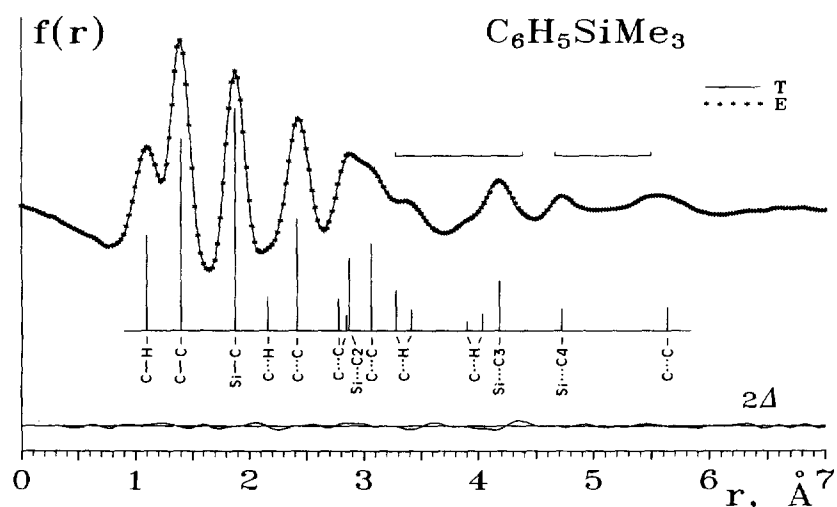
Fig. 2. Radial distribution curves (E, experimental; T, theoretical for the model obtained from refinement C). They were calculated using an artificial damping factor $\exp(-0.002\,s^2)$; theoretical values were used in the $0.00 \le s \le 1.75\,\text{Å}^{-1}$ region. The positions of the most important conformation-independent distances are marked with vertical bars, the heights of which are proportional to the weights of the distances. The regions where contributions from conformation-dependent $C \cdots C$ distances occur are indicated by horizontal lines. Also shown is the difference curve (experimental − theoretical).
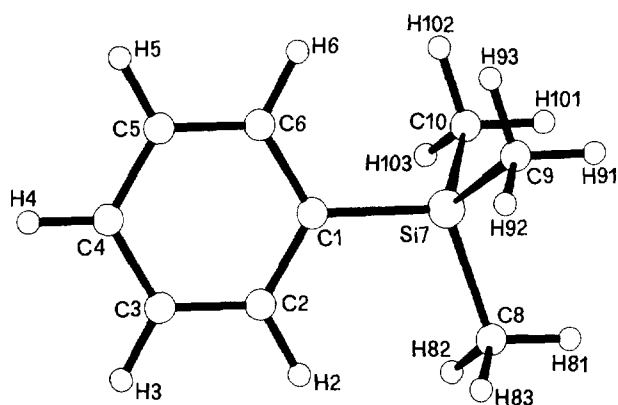

Fig. 3. Numbering of atoms in trimethylsilylbenzene.

different angles of the benzene ring (Fig. 4) are linked by two equations of constraint, expressing the conditions of planarity and ring closure [26]. Thus only five
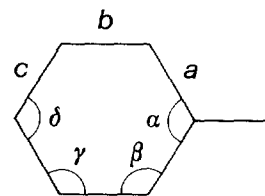

Fig. 4. Lettering of bond distances and angles in a monosubstituted benzene ring of C_{2v} symmetry.

Table 2
Selected geometrical parameters [a] and R factors from refinements A–D [b]

Parameter	Refinements			
	A	B	C	D
$\langle r(\text{C–C})\rangle$	1.4001(3)	1.4001(3)	1.4002(3)	1.4003(3)
$\langle r(\text{Si–C})\rangle$	1.8783(3)	1.8782(3)	1.8782(3)	1.8782(3)
$\langle r(\text{C–H})\rangle$	1.1012(9)	1.1021(10)	1.1020(9)	1.1019(9)
$\angle\text{C2–C1–C6}$ (α)	117.15(14)	117.01(14)	117.17(13)	117.27(14)
$\angle\text{Ph–Si–Me}$	109.4(3)	109.8(2)	109.6(2)	109.8(2)
$\angle\text{Me–Si–Me}$	109.5(3)	109.2(3)	109.4(2)	109.2(2)
$\angle\text{Si–C–H}_{\text{Me}}$	110.7(2)	110.9(2)	110.8(2)	110.6(2)
τ [c]	0.0 [d]	90.0 [d]	76.3(7)	—
R [e]	0.0369	0.0383	0.0370	0.0369

[a] Bond distances r_a are given in ångströms, angles in degrees. Least squares standard deviations are given in parentheses as units in the last digit.
[b] The models adopted in refinements A–D differ in the treatment of the conformation of the molecule. Refinement A: coplanar conformation (1a). Refinement B: perpendicular conformation (1b). Refinement C: the angle of torsion of the SiMe$_3$ group τ was allowed to refine to an effective value. Refinement D: the molecule was assumed to exist as a mixture of four rigid conformers, differing only in the value of τ. More details about the four refinements are given in the text.
[c] Angle of torsion of the SiMe$_3$ group, C2–C1–Si7–C8.
[d] Assumed.
[e] $R = (\Sigma w[I_{\text{obs}} - I_{\text{calc}}]^2/\Sigma w I_{\text{obs}}^2)^{1/2}$.

independent parameters are required to define the ring geometry.

The differences $\Delta_1(\text{C–C})$, $\Delta_2(\text{C–C})$, and $\Delta(\text{C–H})$ were too small to be determined accurately by electron diffraction and were assumed from the MP2 calculations. [3] Attempts to refine $\Delta(\text{Si–C})$ under different refinement conditions led to unacceptable results; thus this difference was also given a fixed value (see Section 4.2). The angle β was assumed to be linearly related to α, according to a well-established empirical relationship that holds for monosubstituted benzene rings with second-row substituents, $\Delta\beta = -0.615\Delta\alpha - 0.384°$ (where $\Delta\alpha$ and $\Delta\beta$ are deviations from 120°) [26].

Eleven mean amplitudes of vibration l were treated as independent variables. They were coupled in groups to other amplitudes with constrained differences Δl. [4] These differences and other fixed amplitudes were mostly taken from spectroscopic calculations based on the MM3 force field [17]. The effects of slightly different choices of Δl values on the geometrical parameters were found to be marginal.

Selected geometrical parameters from four refinements, A–D, are presented in Table 2. The models adopted in refinements A and B correspond to the coplanar (1a) and perpendicular (1b) conformations respectively. In each of these models the vibrational amplitudes for the conformation-dependent distances were given initial values consistent with the respective conformation. (These initial values were estimated by arbitrarily scaling down the corresponding MM3 amplitudes, which were clearly overestimated.) In refinement C the angle of torsion τ of the SiMe$_3$ group was allowed to refine; the initial values of the vibrational amplitudes were averages of the corresponding values for 1a and 1b. The effective value of τ from this refinement is consistent with free rotation, see Section 4.1.

In refinement D the molecule was assumed to exist in the gaseous phase as a mixture of four rigid conformers, differing only in the value of the torsion angle τ.

The four conformers were given τ values of 0, 10, 20, and 30°, and were assigned the respective populations of 0.167, 0.333, 0.333, and 0.167 corresponding to free rotation.

Table 2 shows that the models adopted in refinements A–D fit the experimental data equally well, and yield practically the same geometry. Important molecular parameters from refinement C, corresponding to the average structure of the molecule, are reported in Table 3. We point out that the least squares standard deviations in Tables 2 and 3 should be considered merely as indicators of precision; they are sometimes unrealistically small due to the constraints.

4. Results and discussion

The molecular structure of gaseous trimethylsilylbenzene from electron diffraction is compared with the structures obtained by theoretical calculations in Table 4.

4.1. Molecular conformation

According to theoretical calculations, one of the Si–Me bonds is in the plane of the benzene ring in the equilibrium conformation of the molecule (1a). This conformation, however, is only slightly more stable than the perpendicular conformation (1b). The difference in energy amounts to 0.40 kJ mol^{-1} (MM3), 0.53 kJ mol^{-1} (MO, HF/6-31G* level), or 0.24 kJ mol^{-1} (MO, from MP2 (f.c.)/6-31G* calculations on the HF optimized geometries). MM3 frequency calculations show that 1a corresponds to a local minimum while 1b is a rotational transition state. The latter is characterized as a first-order saddle point by the presence of an imaginary frequency related to the torsion of the substituent about the Si–Ph bond. MM3 calculations, carried out by varying stepwise the angle of torsion from 0° to 30°, [5] show a monotonic increase of the potential energy. Thus the energy difference between 1b and 1a equals the sixfold potential barrier V_6 if higher terms are ignored.

With such a small barrier the conformational space of the molecule is almost evenly populated at the temperature of the electron diffraction experiment. The electron diffraction intensities are fitted equally well by models based on conformations 1a and 1b, and refining the angle of torsion of the SiMe$_3$ group leads to an effective value, $\langle\tau\rangle = 76.3(7)°$, which is about halfway between $\tau = 60°$ (1a) and $\tau = 90°$ (1b), and is thus consistent with free rotation.

[3] The values of $\Delta_1(\text{C–C})$, $\Delta_2(\text{C–C})$, and $\Delta(\text{C–H})$ produced by the MP2 calculations refer to the coplanar conformation of the molecule. The HF calculations, however, indicate that these bond length differences are insensitive to conformational changes.

[4] In the radial distribution the Si7 $\cdots$ C3 and Si7 $\cdots$ C4 peaks show up prominently. Nevertheless, attempts to refine their amplitudes as independent variables led to unsatisfactory results. The values obtained were generally too high and much dependent on the conformation assumed for the molecule. This is probably due to the fact that these peaks contain unresolved contributions from conformation-dependent C $\cdots$ C distances, see Fig. 2. Better results were obtained by coupling $l(\text{Si7} \cdots \text{C2})$, $l(\text{Si7} \cdots \text{C3})$, and $l(\text{Si7} \cdots \text{C4})$ in a single group, including also $l(\text{C1} \cdots \text{C4})$ and $l(\text{C2} \cdots \text{C5})$. The amplitudes of the conformation-dependent distances were grouped in two large blocks: this was done in different ways for the different models adopted in the analysis.

[5] A 30° twist about the Si–Ph bond converts 1a into 1b and vice versa.

Table 3

Molecular parameters of trimethylsilylbenzene from electron diffraction [a]

Distances and mean amplitudes of vibration [b]

Atom pair	Multiplicity	r_a (Å)	l (Å) exp.	calc. [c]	Coupling scheme [b]
C1–C2	2	1.4077(3)	0.0470(5)	0.045	i
C2–C3	2	1.3966(3) [e]	0.0470	0.045	i
C3–C4	2	1.3965(3) [e]	0.0470	0.045	i
Si7–C1	1	1.8751(3)	0.0560(5)	0.052	ii
Si7–C8	3	1.8791(3) [e]	0.0560	0.052	ii
(C–H)$_{Ph}$	5	1.098(1)	0.076(1)	0.077	iii
(C–H)$_{Me}$	9	1.104(1) [e]	0.077	0.078	iii
C1 ⋯ C3	2	2.445(1) [e]	0.058(1)	0.057	iv
C1 ⋯ C4	1	2.845(2) [e]	0.064(1)	0.063	v
C2 ⋯ C4	2	2.429(1) [e]	0.058	0.057	iv
C2 ⋯ C5	2	2.778(1) [e]	0.064	0.063	v
C2 ⋯ C6	1	2.403(2) [e]	0.058	0.057	iv
C3 ⋯ C5	1	2.400(1) [e]	0.058	0.057	iv
Si7 ⋯ C2	2	2.872(1) [e]	0.076	0.075	v
Si7 ⋯ C3	2	4.181(1) [e]	0.073	0.072	v
Si7 ⋯ C4	1	4.720(2) [e]	0.071	0.070	v
C8 ⋯ C1	3	3.067(5) [e]	0.096(2)	0.104	vi
C8 ⋯ C2	1	3.750(8) [e]	0.105(8)	—	vii
C8 ⋯ C3	1	5.005(7) [c]	0.126(11)	—	viii
C8 ⋯ C4	3	5.635(6) [e]	0.150(7)	0.158	ix
C8 ⋯ C5	1	5.202(8) [e]	0.126	—	viii
C8 ⋯ C6	1	4.009(9) [e]	0.105	—	vii
C9 ⋯ C2	1	4.376(4) [e]	0.105	—	vii
C9 ⋯ C3	1	5.489(5) [e]	0.126	—	viii
C9 ⋯ C5	1	4.688(6) [e]	0.126	—	viii
C9 ⋯ C6	1	3.314(6) [e]	0.105	—	vii
C10 ⋯ C2	1	3.462(9) [e]	0.105	—	vii
C10 ⋯ C3	1	4.794(8) [e]	0.126	—	viii
C10 ⋯ C5	1	5.397(5) [c]	0.126	—	viii
C10 ⋯ C6	1	4.259(5) [e]	0.105	—	vii
C8 ⋯ C9	3	3.067(5) [e]	0.095	0.103	vi
C1 ⋯ H2	2	2.168(1) [e]	0.101(4)	0.098	x
C1 ⋯ H3	2	3.433(1) [e]	0.096 [f]	0.096	
C1 ⋯ H4	1	3.943(2) [e]	0.095 [f]	0.095	
C2 ⋯ H3	2	2.161(1) [e]	0.101	0.098	x
C2 ⋯ H4	2	3.427(1) [e]	0.096 [f]	0.096	
C2 ⋯ H5	2	3.876(2) [e]	0.095 [f]	0.095	
C2 ⋯ H6	2	3.403(2) [e]	0.096 [f]	0.096	
C3 ⋯ H2	2	2.158(1) [e]	0.101	0.098	x
C3 ⋯ H4	2	2.174(1) [e]	0.101	0.098	x
C3 ⋯ H5	2	3.398(1) [e]	0.096 [f]	0.096	
C3 ⋯ H6	2	3.876(2) [e]	0.095 [f]	0.095	
C4 ⋯ H2	2	3.417(1) [e]	0.096 [f]	0.096	
C4 ⋯ H3	2	2.161(1) [e]	0.101	0.098	x
Si7 ⋯ H2	2	2.993(1) [e]	0.137	0.145	vi
Si7 ⋯ H3	2	5.033(1) [e]	0.118 [f]	0.118	
Si7 ⋯ H4	1	5.818(2) [e]	0.100 [f]	0.100	
C8 ⋯ H4	3	6.686(6) [e]	0.176(27)	0.187	xi
C1 ⋯ H81	3	4.030(4) [e]	0.124 [f]	0.124	
C1 ⋯ H82	6	3.281(6) [e]	0.215 [f]	0.215	
C4 ⋯ H81	3	6.698(5) [e]	0.162	0.161	xi
C4 ⋯ H82	6	5.576(8) [e]	0.228	0.308	ix
Si7 ⋯ H81	9	2.495(3) [e]	0.116	0.115	iv
C8 ⋯ H91	6	3.279(9) [e]	0.217 [f]	0.217	
C8 ⋯ H92	6	3.281(5) [e]	0.217 [f]	0.217	
C8 ⋯ H93	6	4.031(4) [e]	0.123 [f]	0.123	

Table 3 (continued)

Distances and mean amplitudes of vibration [b]

Atom pair	Multiplicity	r_a (Å)	l (Å)		Coupling scheme [b]
			exp.	calc. [c]	
Angles (deg)					
∠C2–C1–C6 (α)		117.17(13)			
∠C1–C2–C3 (β)		121.36(8) [e]			
∠C2–C3–C4 (γ)		120.8(2) [e]			
∠C3–C4–C5 (δ)		118.46(8) [e]			
∠C1–Si7–C8		109.6(2)			
∠C8–Si7–C9		109.4(2) [e]			
∠Si–C–H$_{Me}$		110.8(2)			
τ [g]		−76.3(7)			
Differences between bond distances (Å)					
Δ_1(C–C) [h]		0.0111 [i]			
Δ_2(C–C) [j]		0.0001 [i]			
Δ(Si–C) [k]		0.0040 [l]			
Δ(C–H) [m]		0.0062 [i]			

[a] Refinement C. Least squares standard deviations are given in parentheses as units in the last digit. [b] To economize on space, the table does not include those C · · · H pairs whose lengths are dependent on the conformation of the molecule. Their amplitudes were coupled with either l(C8 · · · C2) or l(C8 · · · C3). H · · · H pairs are also omitted. [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 MM calculations. [g] Angle of torsion of the SiMe$_3$ group, C2–C1–Si7–C8. [h] Δ_1(C–C) = r(C1–C2) − r(C2–C3). [i] Assumed from ab initio MO calculations (MP2(f.c.)/6-31G* level). [j] Δ_2(C–C) = r(C2–C3) − r(C3–C4). [k] Δ(Si–C) = r(Si7–C8) − r(Si7–C1). [l] Assumed (see text). [m] Δ(C–H) = r(C–H)$_{Me}$ − r(C–H)$_{Ph}$.

This is in contrast with *tert*-butylbenzene, where the higher torsional barrier (V_6 = 2–3 kJ mol^{-1} from theoretical calculations) causes the gas-phase molecules to exist prevalently in the coplanar conformation, as shown by the electron diffraction study [5].

4.2. Geometry of the trimethylsilyl group

The mean length of the four Si–C bonds of the present molecule is determined accurately from electron diffraction. The value obtained, $\langle r_g$(Si–C)$\rangle$ = 1.880 ± 0.004 Å, [6] is in excellent agreement with those reported for other trimethylsilylbenzenes studied by the same technique, see Table 5.

This is not the case, however, for the difference in length between the Si–Me and the Si–Ph bonds, a difference too small to be determined solely by electron diffraction. The theoretical calculations strongly suggest that these bond lengths should differ by no more than a few thousandths of an ångström. The actual difference, Δ(Si–C) = r(Si–Me) − r(Si–Ph), is calculated to be + 0.004 Å by MM3 and − 0.004 Å by MO (HF/6-31G* level), irrespective of the conformation of the substituent. Including electron correlation, the MO calculations yield Δ(Si–C) = − 0.001 Å.

These results are at variance with chemical expecta-

tion. The decrease in the covalent radius of carbon which occurs in going from sp^3 to sp^2 hybridization should make the Si–Ph bond about 0.030 Å shorter than the Si–Me bond. It is well known, however, that additivity of covalent radii does not hold for Si–C bonds. The Si–Me bond in gaseous SiMe$_4$ and Me$_3$Si–SiMe$_3$ is 0.060 ± 0.005 Å shorter than the sum of tetrahedral covalent radii for silicon and carbon [30].

In the course of the analysis it became clear that the value attributed to Δ(Si–C) affects critically the deformation of the benzene ring. Changing the assumed value of Δ(Si–C) from + 0.004 Å to + 0.030 Å under the conditions of refinement C causes the ipso ring angle α to vary from 117.2 to 115.8°. Attributing a reliable value to Δ(Si–C) is thus of utmost importance, and we have adopted the following approach. Table 6 shows the lengths of the Si–Me and Si–Ph bonds in a number of molecules studied by electron diffraction, where (i) either Si–Me or Si–Ph bonds are present, (ii) the Si–C peak of the radial distribution does not contain contributions from other atomic pairs, and (iii) the Si atom is not highly crowded. The bond lengths in Table 6 strongly suggest a small positive value, ca. + 0.004 Å, for the difference Δ(Si–C), in agreement with the results of the MM3 calculations. This value of Δ(Si–C) was adopted in our final refinements.

It has previously been observed for silicon derivatives [11], as well as for other elements such as sulphur [33], that the mean bond length can be determined accurately by electron diffraction while bond length differences may not be very reliable. An extensive

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

Table 4

Molecular geometry [a] of trimethylsilylbenzene: comparison of experimental and theoretical results

Parameter [b]	Electron diffraction [c]	MO calculations (6-31G* basis set) [d,e]		MM3 calculations [e,f,g]
		HF [g]	MP2(f.c.) [h]	
a	1.409 ± 0.003	1.397	1.407	1.411
b	1.398 [i]	1.386	1.396	1.401
c	1.398 [i]	1.385	1.396	1.396
α	117.2 ± 0.2	117.2	117.4	119.0
β	121.4 ± 0.2	121.6	121.5	120.3
γ	120.8 ± 0.2	120.0	120.0	120.2
δ	118.5 ± 0.4	119.6	119.7	120.1
r(Si–Ph)	1.877 ± 0.004	1.897	1.888	1.873
r(Si–Me)	1.881 [i]	1.893	1.887	1.877
∠Ph–Si–Me	109.6 ± 0.4	109.8	109.4	110.2
∠Me–Si–Me	109.4 ± 0.4	109.2	109.5	108.7
r(C–H)$_{Ph}$	1.103 ± 0.003	1.076	1.088	1.103
r(C–H)$_{Me}$	1.109 [i]	1.087	1.095	1.112
∠Si–C–H$_{Me}$	110.8 ± 0.4	111.4	111.2	110.3

[a] Bond distances are given in ångströms, angles in degrees. [b] Bond distances and angles of the benzene ring are lettered according to Fig. 4. [c] From refinement C; bond distances are r_g values. Total errors are given as error limits, and 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 $\Delta/2$ is the effect of the constraints adopted in the refinement [27]. [d] Bond distances are r_e values. [e] Whenever necessary, bond distances and angles have been averaged to be consistent with the symmetry constraints adopted in the electron diffraction study. [f] Bond distances are claimed to be r_g values [28]. [g] Average geometry of the coplanar and perpendicular conformations of the molecule. [h] Coplanar conformation. [i] The differences $a - b$, $b - c$, r(Si–Me) – r(Si–Ph), and r(C–H)$_{Me}$ – r(C–H)$_{Ph}$ have been constrained (see text).

compilation of Si–C bond lengths was communicated in Ref. [11], demonstrating a wide span of Si–C(sp^3) bond lengths between 1.83 and 1.93 Å. This bond length seems to be very sensitive to steric effects and ligand electronegativity. The few available Si–C(aryl) bond lengths cluster around 1.87 Å. So, a priori, it is impossible to say what is the bond length difference between any two Si–C(sp^3) and Si–C(aryl) bonds. This warrants great caution in discussing Si–C bond lengths and suggests the necessity of further study of these bonds.

As regards the Ph–Si–Me, Me–Si–Me, and Si–C–H$_{Me}$ angles, the values from electron diffraction are in close agreement with the corresponding mean values from the ab initio MP2 calculations, see Table 4. As an Si–C bond is more than 0.3 Å longer than a C–C bond, the effect of the phenyl group on the geometry of the trimethylsilyl system in the coplanar conformation of the molecule is expected to be less pronounced than the corresponding effect in *tert*-butylbenzene. The MO calculations (Table 1) indicate that the Si7–C1 bond is tilted from the ring axis by ca. 1.0°, and the C1–Si7–C8 angle is ca. 0.7° larger than the other Ph–Si–Me angles. [7] The corresponding figures for *tert*-butylbenzene are 1.5° and 4° respectively [5].

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[7] The MM3 calculations yield comparable results (tilt of the Si7–C1 bond from the ring axis, 0.8°; enlargment of the C1–S7–C8 angle, 2.5°). Including these distortions in the coplanar model of refinement A does not improve the agreement with the experimental data and has no appreciable effect on the other geometrical parameters.

4.3. Benzene ring geometry

The deformation of the benzene ring in the present molecule follows the pattern expected for an electron-releasing substituent [1,2,34,35]. The most pronounced geometrical variation with respect to benzene occurs at the ipso angle α. The value from electron diffraction, $\alpha = 117.2 \pm 0.2°$, agrees within experimental error with those from MO calculations, 117.2–117.4°. It also agrees with the average solid-state result from a number of molecules containing the C$_6$H$_5$–Si$\leq$ fragment, $\alpha = 117.0(2)°$ [35]. The value from MM3 calculations, 119.0°, is too large, possibly due to inadequacies in the force-field parameters for Si $\cdots$ C interactions.

The bond length changes in the benzene ring caused by the SiMe$_3$ group are less pronounced and could not be determined by electron diffraction. The MO calculations indicate that a is 0.011 Å longer than b, while the difference between b and c is less than 0.001 Å.

The mean length of the ring C–C bonds from electron diffraction, $\langle r_g(C–C)\rangle = 1.402 \pm 0.003$ Å, is accurately determined. It agrees with the value from MM3 calculations, 1.403 Å, claimed [28] also to be an r_g distance. The difference from the value obtained by MO calculations at the HF level, 1.389 Å (6-31G* basis set), may originate from several sources, such as the inherent difference in physical meaning (r_g vs. r_e), basis set limitations, and neglect of electron correlation. Correction for the latter at the MP2(f.c.) level yields $\langle r_e(C–C)\rangle = 1.400$ Å. Comparison with benzene and the other trimethylsilylbenzenes studied by electron

Table 5
Mean lengths (Å) of the Si–C and C–C bonds in trimethylsilylbenzenes from electron diffraction studies

Molecule	$\langle r_g(Si-C) \rangle$	$\langle r_g(C-C) \rangle$	Reference
C_6H_6	—	1.399 ± 0.003	[29]
$C_6H_5-SiMe_3$	1.880 ± 0.004	1.402 ± 0.003	This work
$1,3-C_6H_4(SiMe_3)_2$	1.879 ± 0.004	1.405 ± 0.003	[11]
$1,4-C_6H_4(SiMe_3)_2$	1.880 ± 0.004	1.408 ± 0.003	[8]
$1,3,5-C_6H_3(SiMe_3)_3$	1.881 ± 0.004	1.410 ± 0.003	[11]

Table 6
Si–Me and Si–Ph bond lengths (Å) from electron diffraction studies [a]

Molecule	$r_a(Si-Me)$	$r_a(Si-Ph)$	Reference
$SiMe_4$	1.875(2)	—	[30]
$HSiMe_3$	1.873(6)	—	[31]
$Me_3Si-SiMe_3$	1.877(3)	—	[30]
$S(SiMe_3)_2$	1.871(1)	—	[32]
$SiPh_4$	—	1.869(1)	[10]
$HSiPh_3$	—	1.870(1)	[9]

[a] Included in this table are only those molecules where (i) either Si–Me or Si–Ph bonds are present, (ii) the Si–C peak of the radial distribution does not contain contributions from other atomic pairs, and (iii) the Si atom is not highly crowded.

diffraction (Table 5) shows that the value of $\langle r_g(C-C) \rangle$ increases gradually as the number of $SiMe_3$ groups increases.

The asymmetric attachment of the $SiMe_3$ group to the benzene ring in the coplanar conformation is expected to cause small deviations from axial symmetry in the ring itself [5,36]. These are clearly seen in Table 1: the computed C–C bond distances and C–C–C angles related by the twofold axis differ systematically by 0.002–0.003 Å and 0.1° respectively. The same pattern of differences, though with markedly smaller values, is produced by the MM3 calculations.

With regard to $C-H_{Ph}$ bonds, the MO and MM3 calculations consistently show that the two bonds at the ortho positions, C2–H2 and C6–H6, are bent away from the substituent by about 1.5°, both in the coplanar and in the perpendicular conformation. As with *tert*-butylbenzene [5], the effect is likely to originate from the steric hindrance of the substituent.

5. Supplementary material available

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

Acknowledgements

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