

The Molecular Structures of the Three Disilylbenzenes Determined in the Gas Phase, the Solid State and by *ab initio* Calculations

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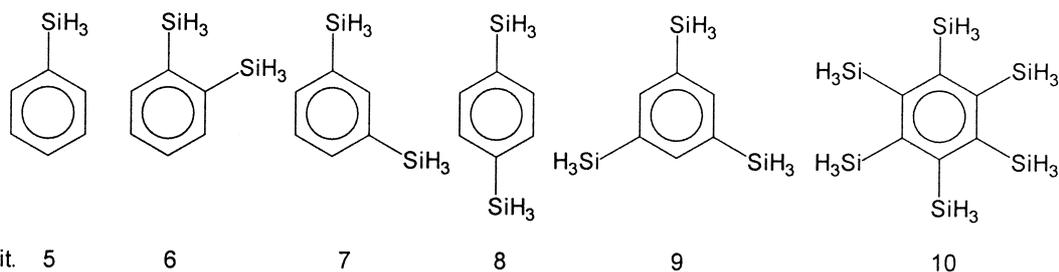
Silylbenzenes, Gas Phase Structure, Electron Diffraction

The molecular structures of four silylbenzenes (benzenes with H₃Si-substituents), *viz.* silylbenzene, 1,2-, 1,3- and 1,4-disilylbenzene, were studied by electron diffraction in the gas phase and by *ab initio* calculations. The structures of 1,2- and 1,4-disilylbenzene were also determined by X-ray diffraction experiments on single crystals grown *in situ*. The results are compared and discussed with the focus on the evaluation of the SARACEN method for the analysis of gas-phase data, and particularly on its ability to deal with small structural distortions. Important experimental structural parameters are the Si-C bond lengths [Å] and the *ipso* C-C-C angles [deg], which are 1.863(3) / 118.2(2) for gaseous silylbenzene (r_{∞}), 1.875(2) / 119.9(2) for gaseous and 1.870(2) / 118.7(av) for solid 1,2-disilylbenzene, 1.871(1) / 119.4(3) for gaseous 1,3-disilylbenzene, 1.870(2) / 119.0(2) for gaseous and 1.866(3) / 117.4(2) for solid 1,4-disilylbenzene. The angle distortions in the benzene ring geometries are analysed and interpreted in terms of an additivity rule of the distortion caused by each of the silyl substituents. This additivity scheme predicts excellently the observed structures of the silylbenzenes and is in best agreement with the structures calculated *ab initio*. The slight distortion of molecular symmetry in the crystal structures makes a detailed comparison of the solid-state values impossible, but on average they are in good agreement with theory and predictions of the additivity model. The gas-phase values obtained by the SARACEN method show less pronounced distortions of the benzene ring geometries than observed or predicted by the other methods, but the trends of distortion are fully consistent.

Introduction

Hydrocarbons with highly hydrogenated silyl functions (SiH₃) have recently been the focus of much interest as precursors to silicon and silicon carbide thin films in chemical vapour deposition

processes [1]. They have also attracted attention as monomers for the production either of polysilanes by dehydrogenative coupling of the Si-H functions (loss of H₂) [2] or of Si/C polymers by desilylative coupling (loss of SiH₄) [3]. Within the group of such hydrocarbons the silylated arenes have a special



Scheme 1.

position as their reactivity is quite different from that of silylated alkanes [4]. Various substitution patterns have been realised for silylated benzenes, which are shown in Scheme 1.

Silylated benzenes have also been the subject of structural investigations and have served as model compounds for study of the deformation of a benzene ring by electropositive substituents [11]. As predicted by a simple version of the VSEPR model, compression of the ring angle at the *ipso* carbon atom is expected upon substitution of an arene H atom by a silyl group. However, in the course of these studies only trialkylsilyl substituents have been involved so far. A systematic study of the structures of silylated arenes with the smallest possible silyl groups has not yet been undertaken. For a study of the undistorted geometry of a molecule, the determination of its gas-phase structure is desirable, but to date the only silylated arene compound studied in the gas phase is silylbenzene (phenylsilane). The structure of this compound was determined by Keidel and Bauer as early as 1956, by the visual method of analysing gas-phase electron-diffraction (GED) patterns [12], and redetermined recently by Domenicano and Hargittai, by state of the art GED techniques [13]. This latest work lead to a surprisingly similar result and bears witness again to the high standards of quality achieved in the early years of electron diffraction.

In this contribution we present the determination of the three possible isomers of disilylbenzene in the gas phase and concurrently the structures of two of these compounds determined in the solid state. Furthermore we present a second redetermination of the structure of gaseous silylbenzene based on more information than was available in the two earlier studies.

Results

In order to get detailed and accurate information about the geometries of the three isomers of disilylbenzene, we have studied these molecules in the solid state, the gas phase and by means of *ab initio* calculations. We were successful in growing single crystals of 1,2-disilylbenzene (ODSB, *ortho*-disilylbenzene) and 1,4-disilylbenzene (PDSB, *para*-disilylbenzene) by *in situ* methods, but we could not obtain single crystalline material of 1,3-disilylbenzene (MDSB, *meta*-disilylbenzene), even by trying various conditions for crystallisation. Crys-

Table 1. Selected geometric parameters for silylbenzene, SB, as determined in the gas phase (GED) and calculated *ab initio*. As the ground state of SB is of C_s symmetry, with the C_6 ring lying in the mirror plane, there are slight deviations of the bond lengths (max. 0.001 Å) and angles (0.4° for Si-C(1)-C(2) 120.8° and Si-C(1)-C(6) 121.2° , otherwise max. 0.1°) from C_{2v} symmetry on which the GED analyses are based because of the freely rotating SiH_3 group. The values given in the table are therefore averaged.

Parameter	GED r_α^0 (this study)	MP2/6- 311G(d,p) r_e	GED r_a [13]
C(1)-C(2)	1.403(3)	1.409	1.410(3)
C(2)-C(3)	1.396(2)	1.399	1.400 ^a
C(3)-C(4)	1.397(3)	1.399	1.400 ^a
Si(7)-C(1)	1.863(3)	1.876	1.870(4)
Si(7)-H	1.466(3)	1.478	1.497(7)
Si-C(1)-C(2)	120.9(2)	121.0	121.0
C(6)-C(1)-C(2)	118.2(2)	118.0	118.1(2)
C(1)-C(2)-C(3)	121.1(3)	121.1	121.1(1)
C(2)-C(3)-C(4)	119.7(4)	120.0	119.9(2)
C(3)-C(4)-C(5)	120.0(5)	119.8	120.0(3)

^a The differences [C(1)-C(2)] – [C(2)-C(3)] and [C(2)-C(3)] – [C(3)-C(4)] have been constrained from the *ab initio* MO calculations.

tallisation experiments with silylbenzene were also unsuccessful, although crystalline material could be obtained, but it obviously undergoes a phase change a few degrees below the melting point. Repeated attempts to circumvent this by crystallising silylbenzene from a pentane solution at lower temperatures, lead to crystalline, but never to single crystalline, material.

Gas-phase structure determinations for all four compounds were carried out by means of electron diffraction. The limitations of structural analyses on electron diffraction data can to some extent be overcome by augmenting the data by restraints derived from *ab initio* calculations of the molecular geometries or vibrational amplitudes in a method, called SARACEN (Structural Analysis Restrained by *ab initio* Calculations for Electron diffraction) [14], a procedure combining and extending Bartell's approach of predicate values [15] and Schäfer's MOCED (Molecular Orbital Constrained Electron Diffraction) method [16]. It should be an interesting test of this method, to see whether it is able to provide us with accurate geometries that even reproduce small differences between bond lengths or bond angles, such as we expect to be present in the three disilylbenzenes. The *ab initio* calculations

Table 2. Selected geometric parameters for 1,2-disilylbenzene, ODSB, as determined in the gas phase (GED), the solid state (XRD) and calculated *ab initio*.

Parameter	GED r_a	MP2/6-311G(d)	XRD
Si(7)-C(2)	1.875(2)	1.883	1.870(2), 1.870(2)
C(1)-C(2)	1.418(3)	1.423	1.410(2)
C(2)-C(3)	1.401(2)	1.409	1.395(3), 1.395(2)
C(3)-C(4)	1.394(2)	1.399	1.380(3), 1.385(3)
C(4)-C(5)	1.389(3)	1.396	1.372(3)
Si(7)-H	1.500(7)	1.483	1.42(3), 1.36(3), 1.35(3)
Si(7)-C(2)-C(1)	123.9(2)	123.5	122.8(1), 123.6(1)
Si(7)-C(2)-C(3)	116.2(2)	117.7	118.4(1), 117.8(1)
C(1)-C(2)-C(3)	119.9(2)	118.8	118.8(1), 118.6(1)
C(2)-C(3)-C(4)	120.0(3)	121.5	121.6(2), 121.3(2)
C(3)-C(4)-C(5)	120.1(3)	119.7	119.6(2), 120.1(2)

used to augment the GED data and to provide an independent source of information for comparison have been carried out at the MP2/6-311G(d) level of theory, which has earlier been shown to produce reliable geometries for arene systems.

We shall discuss the solid-state results first, then turn to the gas-phase structure determinations and *ab initio* calculations and finally compare all the results with one another and with predictions from a simple increment model based on the addition of structural distortions in benzene rings.

Crystal structures. Both ODSB and PDSB crystallise in the monoclinic space group $P2_1/n$. In the case of ODSB the unit cell contains four molecules, with one complete molecule comprising the asym-

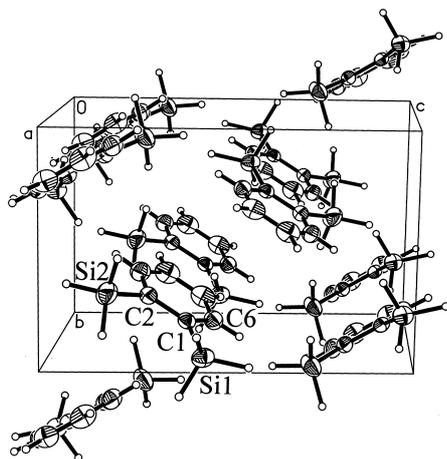


Fig. 1. Packing of molecules of 1,2-disilylbenzene, ODSB, as determined by low temperature crystallography, showing crystallographic numbering.

Table 3. Selected geometric parameters for 1,3-disilylbenzene, MDSB, as determined in the gas phase (GED) and calculated *ab initio*.

Parameter	GED r_a	MP2/6-311G(d)
Si(7)-C(1)	1.871(1)	1.877
C(1)-C(2)	1.404(4)	1.408
C(1)-C(6)	1.404(4)	1.408
C(6)-C(5)	1.393(4)	1.398
Si(7)-H	1.488(6)	1.483
Si(7)-C(1)-C(2)	120.1(2)	120.9
Si(7)-C(1)-C(6)	120.5(2)	121.1
C(2)-C(1)-C(6)	119.4(3)	118.0
C(1)-C(2)-C(3)	120.4(4)	122.2
C(1)-C(6)-C(5)	120.2(3)	120.9
C(6)-C(5)-C(4)	120.4(5)	120.1

Table 4. Selected geometric parameters for 1,4-disilylbenzene, PDSB, as determined in the gas phase (GED), the solid state (XRD) and calculated *ab initio*.

Parameter	GED r_a	MP2/6-311G(d)	XRD
Si(7)-C(1)	1.870(2)	1.877	1.866(3)
C(1)-C(2)	1.405(2)	1.408	1.388(4), 1.386(4)
C(2)-C(3)	1.397(3)	1.398	1.378(3)
Si(7)-H	1.497(6)	1.483	1.33
Si(7)-C(1)-C(2)	120.5(1)	121.1	121.6(2), 121.0(2)
C(6)-C(1)-C(2)	119.0(2)	117.7	117.4(2)
C(1)-C(2)-C(3)	120.5(1)	121.1	121.8(2), 120.9(2)

metric unit, *i.e.* no crystallographic symmetry is imposed on the geometry of the molecule. PDSB has only two molecules per unit cell and the asymmetric unit contains only half a molecule, which therefore has a centre of inversion.

The hydrogen positions for ODSB could be located and refined isotropically, whereas in PDSB the C-bound hydrogen atoms were found and

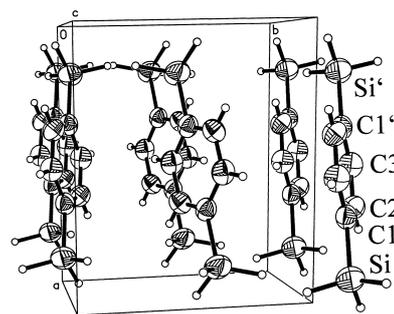


Fig. 2. Packing of molecules of 1,4-disilylbenzene, PDSB, as determined by low temperature crystallography, showing crystallographic numbering.

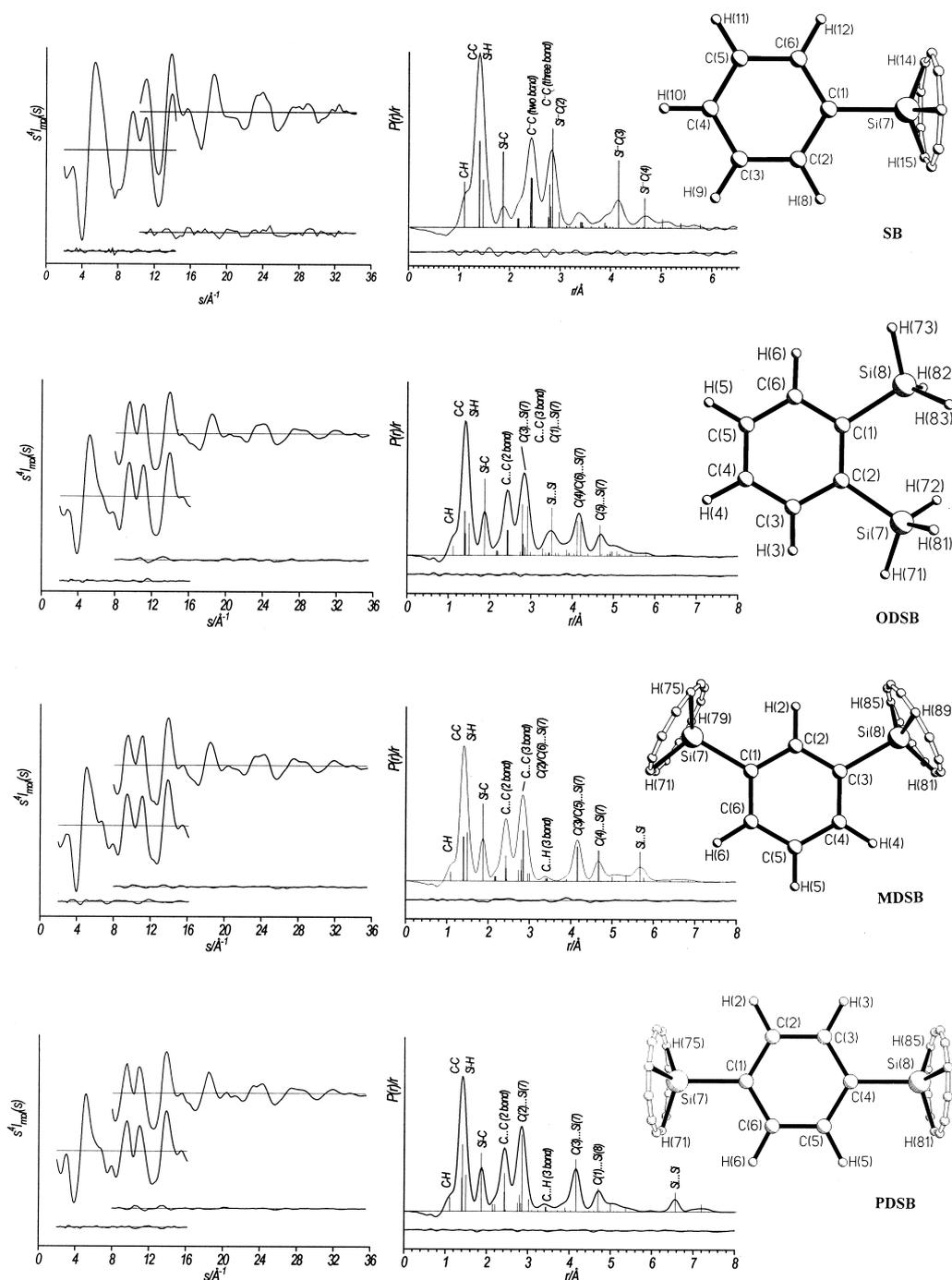


Fig. 3. Experimental and final difference molecular scattering intensity (MIC) curves, experimental and final difference radial-distribution curves (RDC) and molecular structures (including numbering schemes) as obtained by electron diffraction for silylbenzene, SB, 1,2-disilylbenzene, ODSB, 1,3-disilylbenzene, MDSB, and 1,4-disilylbenzene, PDSB. Before Fourier inversion to give the RDC the data were multiplied by $s \cdot \exp[-(0.002 s^2) / (Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{C}} - f_{\text{C}})]$. Vertical lines in the RDC indicate atom pairs, with their heights being proportional to their contributions to the molecular scattering.

refined, but the silyl hydrogen atoms were found to be disordered, and were modelled with six positions about the silicon atom. This is not unexpected, as silyl groups bound to arene rings are known to have very low barriers to rotation (see theoretical section below).

The results of these structure determinations are shown in the plots in Figs. 1 and 2, and the geometric parameters are listed in Tables 3 and 4, together with results from the other methods for comparison. The molecules of ODSB and PDSB pack in the crystal structure in such a way that no significant close contacts between individual atoms of different molecules are observed, which means that the attractive forces that are responsible for forming a solid are van der Waals interactions. Significant contributions of π -stacking can be excluded, as the molecules do not arrange with their rings parallel to those of their neighbours in the structure.

Gas-phase structures. Silylbenzene, SB. As a basis for a systematic investigation of the structures of polysilylbenzenes we undertook a redetermination of the molecular geometry of gaseous silylbenzene. In contrast to the earlier studies, which were based on gas-phase electron-diffraction data and molecular mechanics and *ab initio* constraints, we used a combination of different sources of information, which were gas-phase electron-diffraction intensities, rotational constants from a literature microwave spectroscopy study [17], infrared spectroscopy [18], and *ab initio* calculations. As this combination of techniques undoubtedly leads to improved structural parameters, we shall present the results of this investigation first.

The parameters used to describe the molecular structure of silylbenzene are listed in Table 1 and the final structure and the atom labelling scheme are shown in Fig. 3. All *ab initio* calculations [up to MP2/6-311G(d,p)] predict the global minimum to have C_s symmetry with one silyl hydrogen atom lying in the plane of the benzene ring. The barrier to rotation of the silyl group about the Si-C axis was found in a microwave study to be extremely low [17]. The value that has been given in this contribution is 74 J mol^{-1} . Theoretical calculations of the transition state corresponding to this rotational barrier predict an even smaller value of 11 J mol^{-1} at the MP2/6-31G(d) level (taking zero-point energy into consideration), but the reliability of such calculations is certainly not good enough to com-

Table 5. Independent geometric parameters (r_α^0) for the GED refinements of silylbenzene, SB, and geometric restraints used in the refinement.

No.	Description	$r_\alpha^0/\text{\AA}, \angle/^\circ$	Restraints
p_1	$rC(2)-C(3)$	1.396(2)	
p_2	$rC(1)-C(2) - rC(2)-C(3)$	0.007(5)	0.010(5)
p_3	$rC(3)-C(4) - rC(1)-C(2)$	0.001(5)	0.0(5)
p_4	$rC(1)-Si(7)$	1.863(3)	
p_5	$\angle[C(1)-Si(7)-H(13)]$	111.7(14)	
p_6	$r(Si-H)$	1.466(3)	1.466(3)
p_7	$\angle[C(1)-C(2)-H(8)]$	120.2(13)	119.9(15)
p_8	$r(C-H)$	1.094(4)	
p_9	$\angle[C(1)-C(2)-C(3)]$	121.1(3)	
p_{10}	$\angle[C(2)-C(3)-H(9)]$	121.4(12)	119.9(15)
p_{11}	$\angle[C(6)-C(1)-C(2)]$	118.2(2)	$p_7 - p_{11} = -3.1(5)$

pete with the experimental value here. As both experiment and theory predict the silyl group to be more or less freely rotating at room temperature, at which the electron diffraction experiment was undertaken, our model for silylbenzene contains a freely rotating silyl group described approximately by nine hydrogen positions equally distributed at angle increments of 40° . It should be noted that a structure of silylbenzene with one silyl hydrogen atom oriented so that it has a torsional angle C-C-Si-H of 90.0° (plane H-Si-C perpendicular to the benzene ring plane) has been found to be preferred in a proton magnetic resonance study of a silylbenzene solution in a nematic phase solvent [19].

The geometry of SB was defined by eleven independent parameters (Table 5). The *ipso* C-C-C angle in SB is $118.2(2)^\circ$, which is the same as was found by the earlier GED investigation [$118.1(2)^\circ$] [13]. This value compares fairly well with the one in (trimethylsilyl)benzene [$117.2(2)^\circ$] [11], but is also similar to that in toluene [$118.7(4)^\circ$] [20].

1,2-Disilylbenzene, ODSB. The high volatility of the disilylbenzenes allowed the determination of the geometries of the free molecules by means of gas-phase electron diffraction. For these molecules, rotational constants are not available, nor are stretching frequencies for isolated Si-H bonds known, *i. e.* in SiHD₂ groups. In the case of silyl benzene, the observed infrared absorption for the SiH₃ stretching is close to that of the Si-H bond in C₆H₅SiHD₂. Making the assumption that a similar equivalence is valid for the disilylbenzenes and applying restraints to the Si-H bond distances resulted in changes of the C-C distances of about 0.002 \AA , *i. e.* about one

Table 6. Independent geometric parameters (r_a) for the GED refinements of 1,2-disilylbenzene, ODSB.

No.	Description	$r_a/\text{\AA}$, $\angle/^\circ$
1	$\frac{1}{6}[rC(1)-C(2) + 2rC(2)-C(3) + 2rC(3)-C(4) + rC(4)-C(5)]$	1.400(2)
2	$rSi-C$	1.875(2)
3	$rC(1)-C(2) - \frac{1}{5}[2rC(2)-C(3) + 2rC(3)-C(4) + rC(4)-C(5)]$	0.023(3)
4	$rC(2)-C(3) - \frac{1}{3}[2rC(3)-C(4) + rC(4)-C(5)]$	0.009(2)
5	$rC(3)-C(4) - rC(4)-C(5)$	0.005(3)
6	$rC-H$	1.111(6)
7	$rSi-H$	1.500(7)
8	$\angle SiH_3$ tilt	-1.1(1)
9	$\angle SiH_3$ wag	-2.0(2)
10	$\angle Si-C-C(3)$	116.2(2)
11	$\angle H-Si-C_3$ axis	110.2(12)
12	$\angle SiH_3$ torsion	16.5(19)
13	$\angle C(1)-C(2)-C(3)$	119.9(2)
14	$\angle C(3)-C(4)-C(5)$	120.1(3)
15	$\angle C(2)-C(3)-H(3)$	119.0(10)
16	$\angle C(3)-C(4)-H(4)$	120.3(10)

standard deviation. We chose not to continue to apply such restraints based on assumptions that could not be easily tested.

The model for ODSB was defined in overall C_2 symmetry. The ring geometry was restricted to C_{2v} , except in one refinement described below. The SiH_3 groups were allowed to adopt different C-Si-H angles by using SiH_3 wag/tilt parameters, whereby the SiH_3 wag parameter moves the local C_3 axis in the plane of the ring and the SiH_3 tilt parameter moves the C_3 axis in the plane perpendicular to that of the ring. The total geometry was defined by 16 independent geometrical parameters. Their definitions and values are given in Table 2. The structure was refined using 47 restraints which are explained in Tables 6, the most important being restraints of the C-C-H angles (p_{15} , p_{16}), the differences between the C-C distances (p_3, p_4 , p_5) and the differences between the C-Si-H angles. The amplitude $u(Si \cdots Si)$ was restrained, as it tended to obtain physically insensible values if refined freely. The refinement converged at a final value of $R_G = 5.1\%$ ($R_D = 3.4\%$).

The calculations have shown that the SiCCSi dihedral angle was 3.1° , and in the crystal this angle was 0.8° . In a refinement (r_a) in which the $C_6H_4Si_2$ fragment had C_2 symmetry, the dihedral angle refined to $3.9(40)^\circ$, corresponding to a lengthening of Si...Si by 0.009 Å. The esd of this distance is

Table 7. Independent geometric parameters (r_a) for the GED refinements of 1,3-disilylbenzene, MDSB.

No.	Description	$r_a/\text{\AA}$, $\angle/^\circ$
1	$\frac{1}{3}[rC(1)-C(2) + rC(3)-C(4) + rC(4)-C(5)]$	1.400(1)
2	$rSi-C$	1.871(2)
3	$\frac{1}{2}[rC(1)-C(2) + rC(3)-C(4) - rC(4)-C(5)]$	0.011(1)
4	$rC(1)-C(2) - rC(3)-C(4)$	0.0002(1)
5	$rC-H$	1.092(7)
6	$rSi-H$	1.488(6)
7	$\angle C(6)-C(1)-Si(7)$	120.5(2)
8	$\angle H-Si-C$	108.4(8)
9	$\angle C(1)-C(2)-C(3)$	120.4(4)
10	$\angle C(2)-C(1)-C(6)$	119.4(3)
11	$\angle C(1)-C(6)-H(6)$	121.7(15)

0.015 Å, so the deviation from planarity is not significant, and in the final refinement the out-of-plane parameter was not included.

1,3-Disilylbenzene, MDSB. The model for MDSB was defined assuming C_{2v} symmetry overall. The SiH_3 groups, for which local C_{3v} symmetry was assumed, were modelled as freely rotating by introduction of 12 equally-weighted conformer positions. The total geometry was defined by 11 independent geometrical parameters. Their definition and values are given in Table 3. The structure was refined using 17 restraints, which are explained in Table 7, the most important being restraints on the C-Si-H angles and on the differences between the C-C distances (p_3 and p_4). The refinement converged at a final value of $R_G = 6.3\%$ ($R_D = 4.5\%$).

The Si-C bond length in MDSB is 1.871(1) Å, which is very close to that in the analogous 1,3-bis(trimethylsilyl)benzene, 1.864(4) Å [21]. However, due to the presence of other Si-C bonds in this compound, this distance is not as independently determined as in our case. The *ipso*-C-C-C angles in MDSB are $119.4(3)^\circ$, corresponding to less pronounced benzene ring deformation than in 1,3-bis(trimethylsilyl)benzene, where this angle is smaller, at $116.2(4)^\circ$ [21].

1,4-Disilylbenzene, PDSB. The model for PDSB was defined assuming overall C_{2v} symmetry. As for MDSB, the SiH_3 groups were modelled as freely rotating by introduction of 12 equally-weighted conformer positions. The total geometry was defined by eight independent geometrical parameters. Their definitions and values are given in Table 4. The

Table 8. Independent geometric parameters (r_a) for the GED refinements of 1,4-disilylbenzene, MDSB.

No.	Description	$r_a/\text{\AA}$, \angle°
1	$\frac{1}{3}[rC(1)-C(2) + rC(2)-C(3) + rC(3)-C(4)]$	1.403(1)
2	$r_{\text{Si-C}}$	1.870(2)
3	$rC(1)-C(2) - rC(2)-C(3)$	0.009(5)
4	$r_{\text{C-H}}$	1.104(6)
5	$r_{\text{Si-H}}$	1.497(6)
6	$\angle C(6)-C(1)-C(2)$	119.0(2)
7	$\angle \text{H-Si-C}$	108.9(9)
8	$\angle C(1)-C(2)-\text{H}(2)$	117.9(12)

structure was refined using 11 restraints, which are explained in Table 8, the most important being a restraint on the differences between the C-C distances (p_3). The refinement converged at a final value of $R_G = 5.4\%$ ($R_D = 3.6\%$).

The Si-C bond length in PDSB is 1.870(2) Å (r_a), which is slightly longer than that in the analogous 1,4-bis(trimethylsilyl)benzene [1.854(4) Å, r_a] [22]. However, the problem mentioned for 1,3-bis(trimethylsilyl)benzene regarding the correlation of this parameter with the other Si-C bond lengths in the molecule also applies here. The *ipso*-C-C-C angles in PDSB are 119.0(2)° which corresponds to a much less pronounced benzene ring deformation than in 1,4-bis(trimethylsilyl)benzene, where this angle is smaller at 115.7(4)° [22], although steric arguments can hardly be used to rationalise this.

Ab initio calculations. The lowest energy conformers of the potential energy hypersurfaces for ODSB, MDSB and PDSB were found to be of C_2 , C_2 and D_2 symmetry, respectively. The highest level for geometry optimisations was MP2/6-311G(d). Harmonic frequency calculations on the RHF/6-31G(d) level showed these to be minima and gave low frequencies for MDSB and PDSB at 13 cm⁻¹, which are related to the rotations of the SiH₃ groups about the Si-C axes. Barriers to rotation were calculated for all three compounds, revealing ODSB to be the only one having a slight barrier of 2 kJ mol⁻¹ [MP2/6-31G(d)], which is reasonable, as the two SiH₃ groups are close together and hinder one another in their rotations. The barriers for MDSB and PDSB were found to be negligible compared to the zero-point energies, thus indicating free rotation of these groups. This was taken into consideration in the refinements of the GED data (see above). The force fields computed at the RHF/6-31G(d) level

were used to calculate vibrational amplitudes (using the program ASYM40 [23]) for the purpose of applying them as restraints in the GED refinements in some cases as described above.

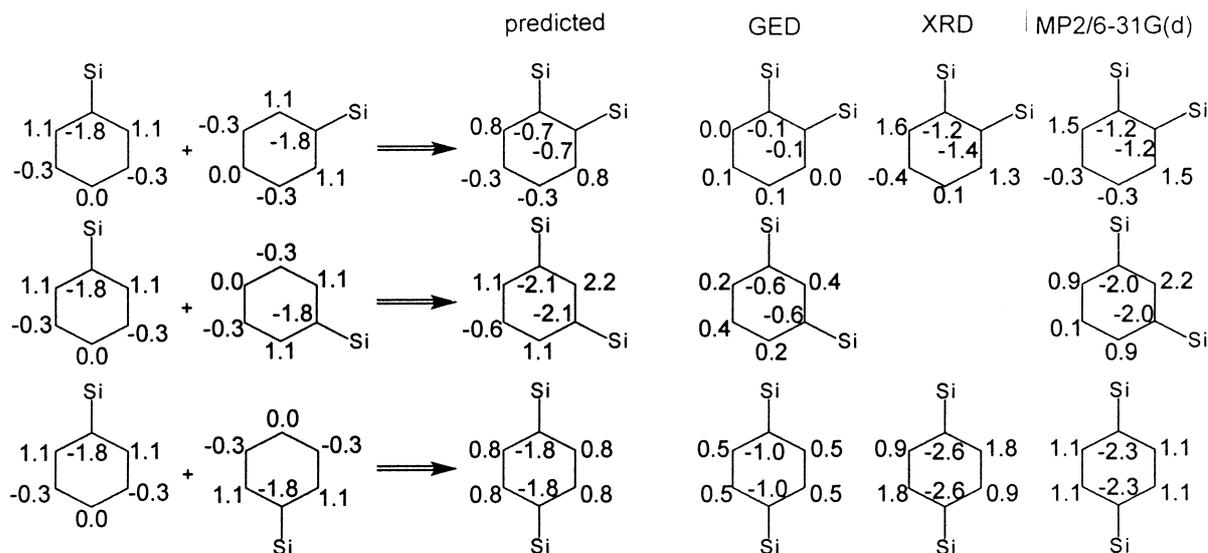
Discussion

Our new parameter values characterising the molecular structure of silylbenzene are listed in Table 1, together with purely theoretical data and the results of the earlier study based solely on GED data [13]. In general we find a reasonable agreement between the structure determinations in the gas phase, the solid state (for ODSB and PDSB) and the *ab initio* calculations. The bond lengths determined by crystallography are generally shorter than those obtained from the GED refinements, while the theoretically calculated ones are almost always the longest. The usual overestimation of bond lengths between second and third row atoms (C-Si) at the MP2 level is also observed in the present investigation. Considering only bond lengths, the agreement between GED parameter values and *ab initio* values is better than any of these with the crystallographic values. The reverse is observed for the bond angles, as the agreement between *ab initio* values and solid-state values is markedly better than between either of them and the gas-phase data.

For ODSB the VSEPR model predicts a compression of the angles at both carbon atoms bearing the silyl groups and a widening of the adjacent C-C distances, which should be most pronounced for the distance C(1)-C(2). In fact this distance is considerably longer (ED 1.418(3) Å, XRD 1.410(2) Å) than the average C-C distance in silylbenzenes or than that in benzene [r_α^0 1.3970(3) Å] [24]. The variation of the C-C distances shows the same pattern for all three methods. However, it has to be noted that the information in the GED structure stems almost completely from the restraints on the differences between the C-C distances taken from the *ab initio* calculations.

The contraction of the *ipso*-C-C-C angles in ODSB is observed in the crystal structure (118.7° on average) and calculated to be almost the same value, whereas the GED refinement shows only a slight, insignificant contraction. The same applies for the consequent widening of the ring angle at C(3) and the slight contraction of that at C(4).

A simple way of predicting the distortions of the benzene ring geometry upon substitution with two



Scheme 2.

silyl groups is to treat the effect of each silyl group independently, *i. e.* to add the angle distortions observed in monosilylbenzene in two different orientations as is depicted in Scheme 2. Our new gas-phase structure for silylbenzene was used as the basis geometry for these predictions, as we can expect this structure to be very reliable because it is based on so many different pieces of experimental and theoretical information.

Comparing the resulting prediction with the actual structures derived by the three methods described above, we see that the predicted structure of ODSB is very well represented by the crystal structure and the *ab initio* calculation, whereas the GED geometry shows less pronounced distortion of the benzene ring geometry as defined in terms of ring angles.

The most pronounced ring distortion is predicted for MDSB, with the C-C-C angle at the atom between the two ipso-C-atoms being widened by 2.2° . This is exactly the value calculated *ab initio* for this compound, but the distortion found in the SARACEN refinement is much less [C-C-C $120.4(4)^\circ$] and not significantly different from an undistorted benzene ring.

It seems unnecessary to repeat this discussion for every detail of the other two disilylbenzenes, MDSB and PDSB, as the results are analogous in their trends and the accuracy of the methods involved. Scheme 2 in itself can be used for a more

in-depth comparison of all parameters. It should, however, be mentioned that the incremental system (see Scheme 2) works well if compared to the *ab initio* values, whereas the relatively small distortions are not so well represented by the GED data, in particular the ring angle distortions. The XRD values show some deviation in themselves, as the maximum possible molecular symmetry is not realised in the crystal structures. The variations in angles related by molecular, but not crystal symmetry shows that distortions of up to at least 1° may be due to packing reasons.

A similar comparison using the distortion of the C-C distances is more complicated, because the distances in the three different methods are physically not the same and thus can not be compared directly.

The repulsion between the silyl groups in ODSB leads to pronounced structure distortions and largely different Si-C-C angles. The differences between the angles Si(7)-C(2)-C(1) and Si(7)-C(2)-C(3) fall over a range of $4 - 6^\circ$ in the solid state and are almost 8° in the gas phase. In MDSB and PDSB, where no such silyl group repulsions occur, the Si-C-C angles on both sides of a Si-C bond are almost equal.

Furthermore, the (Si)C-C(Si) bond in ODSB is markedly lengthened [GED $1.418(3)$, XRD $1.410(2)$ Å] with respect to all other C-C bonds in the four silylbenzene derivatives presented in this contribution. This lengthening is probably also caused by silyl group repulsion and the electronic

Table 9. Experimental conditions (camera distances, nozzle and sample temperatures), data intervals, data ranges and trapezoidal weighting function points, correlation parameters, scale factors, electron wavelengths and final *R* factors for the GED experiments and refinements of the compounds 1,2-disilylbenzene (ODSB), 1,3-disilylbenzene (MDSB) and 1,4-disilylbenzene (PDSB).

Compd	Camera dist. [mm]	T_{samp} [°C]	T_{nozz} [°C]	Δs [Å ⁻¹]	Weighting function [Å ⁻¹]				Corrn. par.	Scale factor	Wavelength [Å]	<i>R</i> Factor [%]
					s_{min}	s_{w1}	s_{w2}	s_{max}				
SB	285.39	20	20	0.2	2.0	4.0	12.2	14.4	-0.007	0.809(6)	0.05691	4.7
	128.36	20	20	0.4	10.4	11.2	30.4	34.4	0.226	0.504(15)	0.05694	
ODSB	746.92	35	52	0.2	2.0	4.0	13.8	16.2	0.427	1.217(13)	0.04866	5.4
	300.63	52	67	0.4	8.0	10.0	30.4	35.6	0.421	0.785(15)	0.04866	
MDSB	746.93	29	52	0.2	2.0	4.0	13.8	16.2	0.485	1.120(9)	0.04866	6.2
	300.63	56	73	0.4	8.0	10.0	30.4	35.6	0.317	0.768(13)	0.04866	
PDSB	746.96	40	53	0.2	2.0	4.0	13.8	16.2	0.422	1.264(10)	0.04866	5.1
	300.63	51	69	0.4	8.0	10.0	30.4	35.6	0.343	0.875(15)	0.04866	

effect of the electropositive Si substituents and is consistently observed by all methods applied.

Conclusion

Our theoretical results on the geometries of the disilylbenzenes are consistent with the predictions of a simple increment model that predicts the benzene ring distortions as an additive effect of the influence that is exerted independently by the two silyl groups. Some deviations from these geometries are observed in our crystallographic results, which are mainly associated with reduced molecular symmetry in the crystal structures, leading to additional small distortions of the molecules. On average these values are close to those from the increment model and those calculated *ab initio*.

The GED/SARACEN structures of the disilylbenzenes show consistently smaller distortions than observed in the other methods, but reflect the same trend for angle widenings and compressions. Either the distortions in the gas phase are smaller than predicted (and smaller than found experimentally in the crystalline phase), or there are systematic vibrational effects that have not been taken into account in the present analysis. It is noteworthy that the experimental distortion in 1,3,5-trisilylbenzenes [25] is smaller than calculated *ab initio*, and in this case the high molecular symmetry rules out the possibility of substantial non-systematic error.

However, the results presented in this contribution show again that using one method alone to determine the structure of a molecule might be misleading even if the distortions are comparably small, but significant in terms of standard deviations. The

Table 10. Selected distances, amplitudes and restraints for the GED refinement of silylbenzene, SB.

No.	Atom pair	Distance	Amplitude	Restraint
1	C2...H8	1.105(4)	0.075(7)	
2	C1...C2	1.404(3)	0.056(6)	
3	C2...C3	1.399(2)	0.055	tied to u_2
4	C3...C4	1.399(3)	0.055	tied to u_2
5	Si7...H13	1.477(3)	0.089(7)	$u_5 = 0.087 \pm 0.009$
6	C1...Si7	1.865(3)	0.072(5)	
7	C2...H9	2.184(13)	0.095(10)	$u_7 = 0.095 \pm 0.010$
8	C1...C3	2.440(3)	0.061(3)	
9	C2...C4	2.419(5)	0.061(3)	$u_9/u_8 = 0.988 \pm 0.050$
10	C3...C5	2.421(6)	0.061(4)	$u_{10}/u_8 = 0.888 \pm 0.044$
11	C2...Si7	2.849(4)	0.087(6)	
12	C2...C6	2.408(6)	0.062(4)	$u_{12}/u_8 = 1.008 \pm 0.050$
13	C1...C4	2.818(5)	0.070(9)	
14	C2...C5	2.789(2)	0.071(9)	$u_{14}/u_{13} = 1.002 \pm 0.050$
15	C3...Si7	4.157(3)	0.104(5)	
16	C4...Si7	4.676(5)	0.085(11)	$u_{16} = 0.130 \pm 0.013$
17	C1...H9	3.441(9)	0.097(9)	$u_{17} = 0.091 \pm 0.009$
18	Si7...H8	2.981(23)	0.156(14)	$u_{18} = 0.148 \pm 0.015$
19	C1...H13	2.771(21)	0.130(13)	$u_{98} = 0.126 \pm 0.013$

results for OSDB lead also to the conclusion that the repulsion between the two SiH₃ groups has no influence on the distortion of the ring geometry. This becomes even more obvious by the fact that the increment model does not take SiH₃ group repulsion into account but predicts the structure distortion of OSDB correctly.

Experimental

The preparation of the compounds was described elsewhere: 1,2-disilylbenzene (ODSB) [6], 1,3-disilylbenzene (MDSB) [7], 1,4-disilylbenzene (PDSB) [8].

Crystal structure determinations of OSDB and PDSB: Single crystals of OSDB and PDSB were grown *in situ*

Table 11. Selected distances, amplitudes and restraints for the GED refinement of 1,2-disilylbenzene, ODSB.

No. Atom pair	Distance	Amplitude	Restraint
1 C-H	1.111(6)	0.066(9)	
2 C(4)-C(5)	1.389(3)	0.051(2)	
3 C(3)-C(4)	1.394(2)	0.051 (tied to u_2)	
4 C(2)-C(3)	1.401(2)	0.051 (tied to u_2)	
5 C(1)-C(2)	1.418(3)	0.051 (tied to u_2)	
6 Si-H	1.500(7)	0.085(7)	
7 Si-C	1.875(2)	0.058(2)	
8 C(1)···C(5)	2.420(5)	0.060(2)	
9 C(3)···C(6)	2.437(6)	0.060 (tied to u_8)	
10 C(1)···C(3)	2.441(4)	0.060 (tied to u_8)	
11 C(3)···Si(7)	2.793(3)	0.077(4)	
12 C(1)···C(4)	2.805(4)	0.069(4)	$u_8/u_{12} = 0.887 \pm 0.044$
13 C(3)···C(6)	2.817(10)	0.068(4)	$u_8/u_{13} = 0.888 \pm 0.044$
14 H(3)···Si(7)	2.857(17)	0.150(15)	$u_{14} = 0.147 \pm 0.015$
15 C(1)···Si(7)	2.914(3)	0.077(4)	
16 Si···Si	3.507(10)	0.164(8)	$u_{16} = 0.130 \pm 0.013$
17 C(4)···Si(7)	4.119(4)	0.077(4)	
18 C(6)···Si(7)	4.204(4)	0.075(4)	
19 C(5)···Si(7)	4.678(3)	0.081(4)	$u_{17}/u_{18} = 1.015 \pm 0.051$

Table 12. Selected distances, amplitudes and restraints for the GED refinement of 1,3-disilylbenzene, MDSB.

No. Atom pair	Distance	Amplitude	Restraint
1 C-H	1.092(7)	0.073(10)	
2 C(4)-C(5)	1.394(1)	0.045(2)	
3 C(3)-C(4)	1.404(1)	0.045 (tied to u_2)	
4 C(1)-C(2)	1.404(1)	0.045 (tied to u_2)	
5 Si-H	1.488(6)	0.080(6)	
6 Si-C	1.871(2)	0.053(2)	
7 C(4)···C(6)	2.418(6)	0.058(2)	
8 C(1)···C(5)	2.424(4)	0.058 (tied to u_7)	
9 C(2)···C(4)	2.425(5)	0.058 (tied to u_7)	
10 C(1)···C(3)	2.437(5)	0.058 (tied to u_7)	
11 C(1)···H(71)	2.733(13)	0.138(12)	$u_{11} = 0.131 \pm 0.013$
12 C(2)···C(5)	2.794(9)	0.066(4)	$u_7/u_{12} = 0.893 \pm 0.045$
13 C(1)···C(4)	2.804(4)	0.066 (tied to u_{12})	
14 C(2)···Si(7)	2.848(2)	0.076(2)	
15 C(6)···Si(7)	2.852(3)	0.076 (tied to u_{14})	
16 H(2)···Si(7)	2.963(4)	0.164(15)	$u_{16} = 0.154 \pm 0.015$
17 H(6)···Si(7)	3.004(26)	0.090(9)	$u_{17} = 0.088 \pm 0.009$
18 C(5)···Si(7)	4.153(4)	0.075(2)	
19 C(3)···Si(7)	4.163(3)	0.075 (tied to u_{18})	
20 C(4)···Si(7)	4.675(3)	0.073(4)	
21 Si···Si	5.675(5)	0.109(5)	

by slowly cooling the melt in a sealed capillary below the melting point of 204(3) and 278(3) K after generation of a suitable seed crystal. Crystal data for ODSB, $C_6H_{10}Si_2$, $M_r = 138.32$, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.3960(9)$, $b = 8.1127(8)$, $c = 12.3291(15)$ Å, $\beta = 95.130(14)$, $V = 836.42(16)$ Å³ at 135(2) K, $\mu = 0.332$ mm⁻¹. $2\theta_{max.} = 60^\circ$, $\omega/2\theta$ -scan, 2830 indep. reflections [$R_{int.} = 0.088$]. Extinction correc-

Table 13. Selected distances, amplitudes and restraints for the GED refinement of 1,4-disilylbenzene, PDSB.

No. Atom pair	Distance	Amplitude	Restraint
1 C-H	1.104(6)	0.085(9)	
2 C(2)-C(3)	1.397(3)	0.048(2)	
3 C(1)-C(2)	1.405(2)	0.048 (tied to u_2)	
4 Si-H	1.497(6)	0.083(5)	
5 Si-C	1.870(2)	0.056(2)	
6 C(2)···C(6)	2.422(3)	0.061(3)	$u_7/u_6 = 0.989 \pm 0.050$
7 C(1)···C(3)	2.433(2)	0.061(2)	
8 C(1)···H(71)	2.748(15)	0.168(14)	$u_8 = 0.158 \pm 0.016$
9 C(2)···C(5)	2.796(3)	0.071(4)	$u_7/u_9 = 0.896 \pm 0.045$
10 C(1)···C(4)	2.824(4)	0.069(4)	$u_7/u_{10} = 0.892 \pm 0.045$
11 C(2)···Si(7)	2.853(2)	0.084(2)	
12 H(2)···Si(7)	3.009(23)	0.192(16)	$u_{12} = 0.189 \pm 0.019$
13 C(3)···Si(7)	4.160(2)	0.075(2)	
14 C(1)···Si(8)	4.694(3)	0.078(4)	
15 Si···Si	6.564(2)	0.084(4)	

Table 14. Rotational constants for silylbenzene applied as restraints in the GED refinement.

Description	Restraint	Uncertainty	Refined value	Difference
A	5702.960	100.0	5361.932	341.027
B	1499.234	0.034	1499.234	0.000
C	1187.058	0.007	1187.058	0.000

Table 15. Further restraints applied in the GED refinement of the structures of 1,2-disilylbenzene, ODSB, 1,3-disilylbenzene, MDSB and 1,4-disilylbenzene, PDSB.

Description	Restraint	Uncertainty	Refined value	Difference
<i>1,2-Disilylbenzene, ODSB:</i>				
$u(C_1 \cdots H_6)$	0.0966	0.0097	0.0974	-0.0008
$u(C_1 \cdots H_6)/u(C_3 \cdots H_4)$	0.9938	0.0497	0.9813	0.0125
$u(C_1 \cdots H_6)/u(C_4 \cdots H_3)$	1.000	0.050	0.9882	0.0118
$u(C_1 \cdots H_6)/u(C_4 \cdots H_5)$	0.999	0.0499	0.9869	0.0121
$u(C_1 \cdots H_6)/u(C_1 \cdots H_3)$	1.0354	0.0518	1.038	-0.0026
$u(C_1 \cdots H_6)/u(C_1 \cdots H_5)$	1.0321	0.0516	1.0356	-0.0035
$u(C_1 \cdots H_6)/u(C_3 \cdots H_5)$	1.0398	0.052	1.0426	-0.0028
$u(C_1 \cdots H_6)/u(C_4 \cdots H_6)$	1.0376	0.0519	1.0396	-0.002
$u(C_1 \cdots H_6)/u(C_1 \cdots H_4)$	1.0376	0.0519	1.0567	-0.0191
$u(C_1 \cdots H_6)/u(C_3 \cdots H_6)$	1.0365	0.0518	1.0537	-0.0172
$u(H_4 \cdots Si_7)$	0.1188	0.0118	0.1143	0.0045
$u(H_6 \cdots Si_7)$	0.1137	0.0114	0.1105	0.0032
$u(H_5 \cdots Si_7)$	0.0998	0.0099	0.1008	-0.001
$u(C_2 \cdots H_{71})$	0.1311	0.0131	0.1353	-0.0042
$u(C_2 \cdots H_{72})$	0.1716	0.0171	0.1745	-0.0029
$u(C_2 \cdots H_{73})$	0.1716	0.0172	0.1746	-0.003
$u(C_2 \cdots H_{81})$	0.2142	0.0214	0.2054	0.0088
$u(C_2 \cdots H_{83})$	0.1273	0.0127	0.1263	0.001
$u(C_2 \cdots H_{82})$	0.1273	0.0127	0.1343	-0.007

tion [ext. coefficient 0.015(4)], no absorption correction. 114 parameters, $R_1 = 0.0454$ for 2441 reflections with F_o

Table 15 (continued).

Description	Re- straint	Uncer- tainty	Refined value	Differ- ence
$u(\text{C}_3\cdots\text{H}_{71})$	0.1625	0.0162	0.163	-0.0005
$u(\text{C}_3\cdots\text{H}_{72})$	0.1938	0.0193	0.1733	0.0205
$u(\text{C}_3\cdots\text{H}_{73})$	0.1938	0.0194	0.1939	-0.0001
$u(\text{Si}_7\cdots\text{H}_{81})$	0.3555	0.0355	0.3515	0.004
$u(\text{Si}_7\cdots\text{H}_{83})$	0.1637	0.0164	0.1658	-0.0021
$u(\text{Si}_7\cdots\text{H}_{82})$	0.250	0.025	0.200	0.050
$u(\text{C}_3\cdots\text{H}_{81})$	0.1991	0.0199	0.1976	0.0015
$u(\text{C}_3\cdots\text{H}_{83})$	0.1409	0.014	0.1426	-0.0017
$u(\text{C}_3\cdots\text{H}_{82})$	0.1409	0.0141	0.1402	0.0007
$u(\text{C}_4\cdots\text{H}_{71})$	0.1673	0.0167	0.172	-0.0047
$u(\text{C}_4\cdots\text{H}_{72})$	0.1971	0.0197	0.1942	0.0029
$u(\text{C}_4\cdots\text{H}_{73})$	0.1971	0.0197	0.1939	0.0032
$u(\text{C}_4\cdots\text{H}_{81})$	0.1693	0.0169	0.1709	-0.0016
$u(\text{C}_4\cdots\text{H}_{83})$	0.1701	0.017	0.1702	-0.0001
$u(\text{C}_4\cdots\text{H}_{82})$	0.1701	0.017	0.1704	-0.0003
p_3	0.0238	0.0031	0.0227	0.0011
p_4	0.0094	0.0017	0.0092	0.0002
p_5	0.0056	0.0027	0.0051	0.0005
p_{16}	120.0	1.00	120.2693	-0.2693
p_{15}	119.7	1.00	118.9878	0.7122
$\angle\text{CSiH}_{71} - \frac{1}{2}[\angle\text{CSiH}_{72}$ $+ \angle\text{CSiH}_{73}]$	-3.22	0.23	-3.2968	0.0768
$\angle\text{CSiH}_{72} - \angle\text{CSiH}_{73}$	-0.78	0.18	-0.7754	-0.0046
<i>1,3-Disilylbenzene, MDSB:</i>				
p_8	110.145	1.000	108.3716	1.7734
$u(\text{C}_1\cdots\text{H}_2)/u(\text{C}_4\cdots\text{H}_5)$	0.995	0.0497	1.0036	-0.0086
$u(\text{C}_1\cdots\text{H}_2)/u(\text{C}_1\cdots\text{H}_6)$	0.745	0.0372	0.7508	-0.0058
$u(\text{C}_1\cdots\text{H}_2)$	0.0964	0.0096	0.0855	0.0109
$u(\text{C}_4\cdots\text{H}_2)/u(\text{C}_1\cdots\text{H}_5)$	0.9979	0.0499	1.0029	-0.005
$u(\text{C}_2\cdots\text{H}_4)/u(\text{C}_4\cdots\text{H}_6)$	0.8912	0.0446	0.8876	0.0036
$u(\text{C}_4\cdots\text{H}_2)/u(\text{C}_2\cdots\text{H}_4)$	0.5986	0.0299	0.5919	0.0067
$u(\text{C}_4\cdots\text{H}_2)$	0.0932	0.0093	0.0937	-0.0005
$u(\text{Si}_7\cdots\text{H}_5)$	0.1197	0.0119	0.1161	0.0036
$u(\text{C}_1\cdots\text{H}_4)$	0.1688	0.0168	0.1475	0.0213
$u(\text{Si}_7\cdots\text{H}_4)$	0.1881	0.0188	0.1772	0.0109
p_3	0.0114	0.0012	0.0112	0.0002
p_4	0.0003	0.0001	0.0002	0.0001
<i>1,4-Disilylbenzene, PDSB:</i>				
$u(\text{C}_1\cdots\text{H}_2)$	0.0966	0.0096	0.0999	-0.0033
$u(\text{Si}_7\cdots\text{H}_3)$	0.1321	0.0123	0.1314	0.0007
$u(\text{C}_5\cdots\text{H}_2)$	0.0735	0.0073	0.0736	-0.0001
$u(\text{H}_{71}\cdots\text{H}_{75})$	0.150	0.015	0.147	0.003
$u(\text{C}_1\cdots\text{H}_2)/u(\text{C}_1\cdots\text{H}_3)$	1.035	0.0517	1.0243	0.0107
$u(\text{C}_1\cdots\text{H}_2)/u(\text{C}_2\cdots\text{H}_6)$	1.048	0.0524	1.0339	0.0141

$> 4 \sigma(F_o)$ and $wR_2 = 0.1127$ for all 2656 data. Crystal data for PDSB, $\text{C}_6\text{H}_{10}\text{Si}_2$, $M_r = 138.32$, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.0646(11)$, $b = 7.4787(12)$, $c = 6.2845(10)$ Å, $\beta = 95.904(16)$, $V = 423.78(11)$ Å³ at 205(2) K, $\mu = 0.338$ mm⁻¹. $2\theta_{\text{max}} = 60^\circ$, $\omega/2\theta$ -scan, 1750 indep. reflections [$R_{\text{int}} = 0.046$]. No extinction or absorption correction. 49 parameters, $R_1 = 0.0541$ for 1235 reflections with $F_o > 4 \sigma(F_o)$ and $wR_2 = 0.1368$ for all 1638 data. Solution (direct methods) and

Table 16. Correlation matrix elements ($\times 100$) with absolute values > 50 for the least squares refinements of SB. k_1 and k_2 denote scaling factors.

p_2	p_3	p_5	p_8	u_{10}	u_{14}	u_{15}	k_1	k_2	
-71	-72								p_1
		-57							p_4
			-59						p_7
							-55		p_{11}
								58	u_1
					-64	-64			u_7
				58					u_{12}
				59					u_{13}
					100	92			u_{14}

Table 17. Correlation matrix elements ($\times 100$) with absolute values > 50 for the least squares refinements of ODSB. The Table is split in two parts. k_1 and k_2 denote scaling factors.

p_7	p_{13}	p_{14}	p_{10}	k_1	k_2	
-61		73				p_1
	61					p_2
			-66			p_{13}
				51		$u(\text{Si-H})$
					62	k_1

refinement were performed using the program SHELXTL 5.01 [26].

Gas-phase electron diffraction. Electron scattering intensity data for SB were recorded on Kodak Electron Image plates using the Edinburgh diffraction apparatus [27] operating at 40 kV acceleration voltage. Two data sets at different camera distances were recorded for each compound from three exposures at each camera distance. Diffraction patterns of benzene were recorded concurrently for the purpose of calibration of wavelengths.

Electron scattering intensity data for ODSB, MDSB and PDSB were recorded on Kodak Electron Image film using the Oregon State University diffraction apparatus operating at 60 kV acceleration voltage. Two data sets at different camera distances were recorded for each compound from three exposures. Diffraction patterns of CO_2 were recorded concurrently for the purpose of wavelength-calibration.

The least-squares refinements were carried out using the program ED96 [28] using the scattering factors established by Fink and co-workers [29]. The refined molecular parameters, their definition and the applied restraints, a list with selected interatomic distances including vibrational amplitudes and applied restraints are listed in Tables 10 - 19.

Ab initio calculations. *Ab initio* molecular orbital calculations were carried out using the Gaussian 98 pro-

Table 17 (continued).

<i>U</i>	<i>U</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	
(C ₁ ·C ₂)	(C ₃ ·H ₄)	(C ₄ ·H ₃)	(C ₄ ·H ₅)	(C ₄ ·Si ₇)	(C ₆ ·Si ₇)	(C ₁ ·H ₃)	(C ₁ ·H ₅)	(C ₃ ·H ₅)	(C ₄ ·H ₆)	(C ₁ ·H ₄)	(C ₃ ·H ₆)	(Si-H)		
-55													79	<i>p</i> ₁
														<i>p</i> ₇
	74	74	74		-55	-53							71	<i>p</i> ₁₄
		55	54				76	76	76	76	77	77		<i>u</i> (C ₁ ·H ₆)
			55				56	56	56	56	57	57		<i>u</i> (C ₃ ·H ₄)
							57	57	57	57	57	57		<i>u</i> (C ₄ ·H ₃)
							56	56	56	56	57	57		<i>u</i> (C ₄ ·H ₅)
						58								<i>u</i> (C ₄ ·Si ₇)
								57	57	57	58	58		<i>u</i> (C ₁ ·H ₃)
									57	57	58	58		<i>u</i> (C ₁ ·H ₅)
										57	58	58		<i>u</i> (C ₃ ·H ₅)
											58	58		<i>u</i> (C ₄ ·H ₆)
												59		<i>u</i> (C ₁ ·H ₄)

Table 18. Correlation matrix elements ($\times 100$) with absolute values > 50 for the least squares refinements of MDSB.

<i>p</i> ₉	<i>p</i> ₇	<i>p</i> ₁₀	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	
			(C ₁ ·H ₆)	(C ₄ ·H ₅)	(C ₂ ·H ₄)	(C ₄ ·H ₆)	(Si-H)		
-57	57							58	<i>p</i> ₁
-65									<i>p</i> ₂
	52-93								<i>p</i> ₉
	-62								<i>p</i> ₇
		85	85						<i>u</i> (C ₁ ·H ₂)
			73						<i>u</i> (C ₁ ·H ₆)
				81					<i>u</i> (C ₄ ·H ₂)
					55				<i>u</i> (C ₁ ·H ₅)

gram [30]. Geometry optimisations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G [31] and 6-31G(d) [32] 6-311G(d) [33] basis sets, while the larger was used for calculations at the MP2 level of theory.

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Table 19. Correlation matrix elements ($\times 100$) with absolute values > 50 for the least squares refinements of PDSB.

<i>p</i> ₇	<i>p</i> ₂	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>	<i>k</i> ₂	
		(C ₁ ·C ₄)	(C ₁ ·H ₃)	(C ₂ ·H ₆)	(C ₂ ·C ₅)		
-57							<i>p</i> ₃
	64						<i>p</i> ₇
			73	73			<i>u</i> (C ₁ ·H ₂)
		56			53		<i>u</i> (C ₁ ·H ₃)
				51			<i>u</i> (C ₁ ·H ₃)
						52	<i>k</i> ₁

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- [1] W. S. Rees (ed.): CVD of Nonmetals, VCH, Weinheim (1996).
 [2] a) C. T. Aitken, J. F. Harrod, E. Samuel, *Can. J. Chem.* **64**, 1977 (1986); b) H.-G. Woo, J. F. Walter, T. D. Tilley, *Macromolecules* **24**, 6836 (1991).
 [3] T. Sakakura, O. Kumberger, R. P. Tan, M.-P. Arthur, M. Tanaka, *J. Chem. Soc. Chem. Commun.* 193 (1995).

- [4] a) M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, John Wiley & Sons, New York (2000); b) W. Beyer, R. Hager, H. Schmidbaur, G. Winterling, *Appl. Phys. Lett.* **54**, 1966 (1989); c) H. Schmidbaur, J. Zech, *Eur. J. Solid State Inorg. Chem.* **29**, 5 (1992); d) R. Hager, O. Steigelmann, G. Müller, H. Schmidbaur, H. E. Robertson, D. W. H. Rankin, *Angew. Chem. Int. Ed. Engl.* **29**, 201 (1990).

- [5] M. C. Harvey, W. H. Nebergall, J. S. Peake, *J. Am. Chem. Soc.* **79**, 1437 (1957).
- [6] a) S. Shimada, M. Tanaka, K. Honda, *J. Am. Chem. Soc.* **117**, 8289 (1995); b) R. Schröck, K. Angermaier, A. Sladek, H. Schmidbaur, *Z. Naturforsch.* **50b**, 613 (1995).
- [7] M. Ishikawa, E. Toyoda, M. Ishii, A. Kunai, Y. Yamamoto, M. Yamamoto, *Organometallics* **13**, 808 (1994).
- [8] D. R. Anderson, J. M. Holovka, *J. Chem. Soc.* 2269 (1965).
- [9] K. Shea, D. A. Loy, *Chem. Mater.* **1**, 572 (1989).
- [10] C. Rüdinger, H. Beruda, H. Schmidbaur, *Chem. Ber.* **125**, 1401 (1992).
- [11] A. R. Campanaelli, F. Ramondo, A. Domenicano, I. Hargittai, *J. Organomet. Chem.* **537**, 309 (1997).
- [12] F. A. Keidel, S. H. Bauer, *J. Chem. Phys.* **25**, 1218 (1956).
- [13] G. Portalone, F. Ramondo, A. Domenicano, I. Hargittai, *J. Organomet. Chem.* **560**, 183 (1998).
- [14] a) A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson, B. A. Smart, *J. Phys. Chem.* **100**, 12280 (1996); b) N. W. Mitzel, B. A. Smart, A. J. Blake, H. E. Robertson, D. W. H. Rankin, *J. Phys. Chem.* **100**, 9339 (1996).
- [15] L. S. Bartell, D. J. Romenensko, T. C. Wong (eds): *Molecular Structure by Diffraction Methods, Specialist Periodical Reports, The Chemical Society* vol. 3, p. 72 (1975).
- [16] V. J. Klimkowski, J. D. Ewbank, C. Van Alsenoy, J. N. Scarsdale, L. Schäfer, *J. Am. Chem. Soc.* **104**, 1476 (1982).
- [17] a) W. Caminati, G. Cazzoli, M. Mirri, *Chem. Phys. Lett.* **35**, 475 (1975); b) J. W. Fleming, C. N. Banwell, *J. Molec. Spectrosc.* **31**, 318 (1969); c) J. R. Durig, K. L. Hellams, J. H. Mulligan, *Spectrochim. Acta* **28A**, 1039 (1972).
- [18] D. C. McKean, I. Torto, *J. Mol. Spectrosc.* **152**, 389 (1992).
- [19] C. L. Khetrapal, E. D. Becker, *J. Magn. Reson.* **43**, 8 (1981).
- [20] A. Domenicano, G. Schultz, M. Kolonits, I. Hargittai, *J. Mol. Struct.* **53**, 197 (1979).
- [21] B. Rozsondai, I. Hargittai, *J. Organomet. Chem.* **436**, 127 (1992).
- [22] B. Rozsondai, B. Zelei, I. Hargittai, *J. Mol. Struct.* **95**, 187 (1982).
- [23] L. Hedberg, I. M. Mills, ASYM20, ASYM40, Programs for Force Constants and Normal Coordinate Analysis, Version 3.0, June 1994; see also L. Hedberg, I. M. Mills, *J. Mol. Spectrosc.* **160**, 117 (1993).
- [24] O. E. K. Moe, T. G. Strand, *J. Mol. Struct.* **128**, 13 (1985).
- [25] N. W. Mitzel, S. L. Hinchley, D. W. H. Rankin, unpublished results (2001).
- [26] SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc. Madison, WI (1995).
- [27] C. M. Huntley, G. S. Laurensen, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.* 945 (1980).
- [28] N. W. Mitzel, P. T. Brain, D. W. H. Rankin, ED96, Version 2.0 (1998); A program developed on the basis of formerly described ED programs: A. S. F. Boyd, G. S. Laurensen, D. W. H. Rankin, *J. Mol. Struct.* **71**, 217 (1981).
- [29] A. W. Ross, M. Fink, R. Hilderbrandt, in A. J. C. Wilson (ed.): *International Tables for X-Ray Crystallography*, Vol. C., p. 245, Kluwer Academic Publishers, Dordrecht, Boston (1992).
- [30] Gaussian 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, (Jr.), R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA (1998).
- [31] a) J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **102**, 939 (1980); b) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.* **104**, 2797 (1982); c) W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, J. S. Binkley, *J. Am. Chem. Soc.* **104**, 5039 (1982).
- [32] a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972); b) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).