

The experimental gas-phase structures of 1,3,5-trisilylbenzene and hexasilylbenzene and the theoretical structures of all benzenes with three or more silyl substituents†

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The structures of 1,3,5-trisilylbenzene and hexasilylbenzene in the gas phase have been determined by electron diffraction, and that of 1,3,5-trisilylbenzene by X-ray crystallography. The structures of three trisilylbenzene isomers, three tetrasilylbenzenes, pentasilylbenzene and hexasilylbenzene have been computed, *ab initio* and using Density Functional Theory, at levels up to MP2/6-31G*. The primary effect of silyl substituents is to narrow the ring angle at the substituted carbon atoms. Steric interactions between silyl groups on neighbouring carbon atoms lead first to displacement of these groups away from one another, and then to displacement out of the ring plane, with alternate groups moving to opposite sides of the ring. In the extreme example, hexasilylbenzene, the SiCCSi dihedral angle is 17.8(8)°.

Introduction

The deformations of benzene rings caused by substituents have been investigated by various structural methods; examples of studies include some by gas-phase electron diffraction (GED),¹ X-ray crystallography,² microwave spectroscopy^{3–5} and *ab initio* molecular orbital (MO) calculations.¹ Changes in ring bond lengths and internal ring angles have been attributed primarily to the electronic nature of the substituents. Those that are σ -accepting lead to widening of the internal ring angle (α) at the position (*ipso*) at which they are bonded and a decrease in the two adjacent (β) angles. In addition to the σ -inductive effect, deformations can be caused if the substituent has the ability to share π electrons with the ring system; the greater the extent of conjugation, the smaller the α angle becomes, although this effect is less pronounced than the σ effect.

Substituents that are σ donors, such as silyl groups, are much less frequently encountered, but they cause the opposite effects to be observed. Narrowing of the *ipso* angle may be associated with increase in carbon 2p orbital character in these bonds, and a consequence of this could be displacement of the carbon-substituent bond from the ring plane as the hybridisation shifts from sp^2 more towards sp^3 . Alternatively, if the effect was less pronounced, the equilibrium arrangement could remain planar, but the out-of-plane deformation potential could be shallow.

Such structural changes are, in general, small and require careful and accurate experimental work if they are to be measured reliably. This is certainly true for derivatives containing silyl groups, which are the only σ -donating ones for which many different compounds are available, with from one to six substituents. The structure of silylbenzene (phenyl silane) has been determined three times now by GED; by Keidel and Bauer in 1956,⁶ by Domenicano and Hargittai⁷ and most recently by Mitzel *et al.*¹ The structures of the three disilylbenzenes (1,2-disilylbenzene, 1,3-disilylbenzene and 1,4-disilylbenzene) have also been recently investigated by Mitzel *et al.*¹

In the work we describe here we have applied GED to the two molecules with silyl substituents that have the highest symmetry, and are therefore most suitable for very precise determination of the effects of these substituents. These compounds are 1,3,5-trisilylbenzene and hexasilylbenzene. The experimental investigations have been complemented by theoretical studies, which have been extended to the other benzene derivatives with three or more silyl groups, *i.e.* 1,2,3-trisilylbenzene, 1,2,4-trisilylbenzene, 1,2,3,4-tetrasilylbenzene, 1,2,3,5-tetrasilylbenzene, 1,2,4,5-tetrasilylbenzene and pentasilylbenzene. We have used the structural data with an additive model, in which the distortions of the structure of the mono-substituted silylbenzene¹ from a regular hexagon are used as a template to predict the structures of the di-, tri-, tetra-, penta- and hexa-substituted compounds, for comparison with the computed structures.

Experimental

Samples of 1,3,5-trisilylbenzene and hexasilylbenzene were prepared and purified by published methods.^{8,9}

Theoretical methods

All calculations were performed on DEC Alpha APX 1000 and Alpha Server 1000A workstations using the GAUSSIAN94¹⁰ and GAUSSIAN98¹¹ programs. Series of geometry optimisations were undertaken for the tri-, tetra-, penta- and hexasilylbenzenes to locate all possible conformations and to gauge the effect of improvements to basis set and level of theory. An extensive search of each potential energy surface was carried out using the HF/3-21G*^{12–14} and HF/6-31G*^{15–17} level of theory and basis sets. The search located conformers with C_{3h} (1,3,5-trisilylbenzene), C_s (1,2,3-trisilylbenzene) and C_1 (1,2,4-trisilylbenzene) symmetry as being the lowest in energy for the trisilylbenzenes; with C_2 (1,2,3,4-tetrasilylbenzene), C_s (1,2,3,5-tetrasilylbenzene) and C_{2h} (1,2,4,5-tetrasilylbenzene) symmetry for the tetra-substituted compounds, while penta- and hexasilylbenzene were found to have C_s and D_{3d} symmetry,

† Electronic supplementary information (ESI) available: Tables S1–S3 and Figs. S1–S2. See <http://www.rsc.org/suppdata/dt/b5/b503637b/>

respectively. Further calculations were then performed on these structures at MP2 and B3LYP levels of theory using the 6-31G* basis set. The basis sets used are available in both versions of GAUSSIAN. Frequency calculations were carried out for each compound at the HF and B3LYP levels of theory in order to determine the nature of the stationary points located on the potential energy surface. The force constants obtained from the B3LYP calculations for 1,3,5-trisilylbenzene and hexasilylbenzene were subsequently used in conjunction with an appropriate set of pseudo-symmetry co-ordinates, as detailed by Pulay,¹⁸ in the construction of harmonic force fields for these compounds using the program ASYMX.¹⁹ Since no experimental vibrational spectra were available, the force fields were scaled by a factor of 0.96, to compensate for the theoretical overestimation of harmonic vibrational frequencies.²⁰

The optimised lowest-energy structures and atom numbering schemes for all of the silyl benzenes are shown in Fig. 1.

Gas-phase electron diffraction (GED)

Electron scattering intensities for 1,3,5-trisilylbenzene and hexasilylbenzene were recorded on Kodak Electron Image plates using the Edinburgh apparatus²¹ operating at 40 kV. Six plates were recorded for each compound, three at the long camera distance and three at the short distance, and then traced digitally using a PDS densitometer at the Institute of Astronomy in Cambridge, with a scanning program described elsewhere.²² To calibrate the experiment, the scattering patterns of benzene were also recorded and analysed in the same way, thus eliminating any systematic errors in the electron wavelength and camera distances. Data reduction and least-squares refinements were carried out using the program 'ed@ed' program,²³ employing the scattering factors of Ross *et al.*²⁴ Experimental parameters, namely temperatures, nozzle-to-plate distances, weighting functions for creating the off-diagonal weight matrix, correlation parameters, final scale factors and electron wavelengths, for both compounds are listed in Table 1.

GED molecular model: 1,3,5-silylbenzene

As silyl groups attached to arene rings are known to have low barriers to rotation (74 J mol⁻¹ for silylbenzene²⁵⁻²⁷) and in light of the low frequencies of silyl torsional modes identified by the *ab initio* study (13.7 cm⁻¹), two models were written. In one the silyl groups were treated statically, while in the other (dynamic) model the free rotation of each group was approximated by a total of 12 hydrogen atom positions, each with a weight of 0.25. For the static model, six independent geometrical parameters were required to model 1,3,5-trisilylbenzene completely in the predicted C_{3h} symmetry: two bond lengths, an average of two bond lengths and the difference between them, and two bond angles. An additional parameter was also included to allow torsional twisting of the silyl group about the Si–C bond.

Table 1 Nozzle-to-plate distances (mm), weighting functions (nm⁻¹), correlation parameters, scale factors and electron wavelengths (pm) used in the electron-diffraction study

	1,3,5-Trisilylbenzene		Hexasilylbenzene	
Nozzle-to-plate distance ^a	96.57	261.02	92.60	261.01
ΔS	4	2	4	2
S_{min}	100	20	100	20
S_{w1}	120	40	130	40
S_{w2}	304	130	296	128
S_{max}	356	140	348	150
Correlation parameter	0.1562	0.4418	0.1929	0.3908
Scale factor ^b	0.523(14)	0.751(3)	0.814(25)	0.865(14)
Electron wavelength	6.016	6.016	6.016	6.016

^a Determined by reference to the scattering pattern of benzene vapour.

^b Values in parentheses are the estimated standard deviations.

Although this lowers the symmetry to C₃, it may improve the results of the final refinement by allowing for torsional motions. The CSiH₃ groups were modelled assuming local C_{3v} symmetry. The bond lengths were the average of C–C and Si–H, p_1 , the difference between the two, p_2 , Si–C, p_3 and C–H, p_4 . The angle parameters consisted of the C–C–C angle (at the silyl substituent), p_5 , and the C–Si–H angle, p_6 . The silyl twisting parameter, p_7 , is defined as the clockwise rotation of all three silyl groups from an initial position in which one of the silyl hydrogens of each group lies in the plane of the ring and the molecule overall has C_{3h} symmetry. In the dynamic case, only six parameters were required to define the structure adequately. These are identical to the first six mentioned above. In this case, however, the final twisting parameter is redundant as each silyl group contains 12 equally spaced hydrogens at 30° angular increments, representing free rotation.

GED molecular model: hexasilylbenzene

Only one model, with seven independent geometrical parameters, was required to model hexasilylbenzene in D_{3d} symmetry. In this case, the crowding caused by groups on adjacent ring positions restricts rotation of the silyl groups, so that the lowest calculated (ring torsion) frequency (B3LYP/6-31G* level) for hexasilylbenzene is 48.1 cm⁻¹, compared to 13.7 cm⁻¹ for 1,3,5-trisilylbenzene. Again, the CSiH₃ groups were assumed to have local C_{3v} symmetry. The bond length parameters were C–C, p_1 , Si–C, p_2 , and Si–H, p_3 , and bond angles were C–C–C, p_4 , and H–Si–H, p_5 . Note that in D_{3d} symmetry the angles C–C–C may be less than 120°, if the ring is non-planar. An angle parameter, p_6 , was required to describe bending of the C–Si bonds out of the plane of the ring. Allowing for the possible puckering of the ring, this parameter is defined as the angle between each Si–C bond and a plane perpendicular to the molecular three-fold axis (Fig. 2). In addition, the silyl groups have a tilt parameter, p_7 , which tilts the groups in the σ_v planes (Fig. 2). Positive tilt values indicate that the silyl groups are tilted in the same direction as the silicon atom is displaced by a positive out-of-plane angle, p_6 .

Crystal structure determination of 1,3,5-trisilylbenzene

A crystal of 1,3,5-trisilylbenzene was grown *in situ* by establishing a solid/liquid equilibrium, selecting of a suitable seed crystal by melting the rest of the solid followed by slowly cooling the melt until the growing crystal filled the whole capillary. Crystal data: C₆H₁₂Si₃, $M_r = 168.43$, $T = 140(2)$ K, tetragonal, space group $P4_2/mbc$, $a = b = 11.3393(6)$, $c = 16.3909(14)$ Å, $V = 2107.5(2)$ Å³, $Z = 8$, $\rho = 1.062$, $\mu(0.71073 \text{ \AA}) = 0.382 \text{ mm}^{-1}$, $\theta_{max} = 25.01^\circ$. Reflections collected 1855, unique 964 [$R_{int} = 0.0563$]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically. The SiH₃ hydrogen atoms were placed in positions of idealised tetrahedral angles and refined with a common Si–H bond length with the displacement parameters tied to that of the adjacent silicon atom. The SiH₃ group at Si(1) was modelled with two split positions of the H atoms. $R_1 = 0.0575$ [for 545 data with $I > 2\sigma(I)$], $wR_2 = 0.1764$ (all 964 data).

Results

Ab initio MO and DFT calculations

The geometrical parameters were found to be largely unaffected by changes in level of theory and basis-set quality. DFT calculations gave results comparable to those obtained at the MP2 level, although, in the case of 1,3,5-benzene and hexasilylbenzene, for which gas-phase experimental data were available, the MP2 results were closer to those of the GED refinement. In general, it was found that the C–Si bond lengths shortened while the C–H and C–C bonds lengthened as the calculations improved. MP2 calculations, although closest to the GED experiments,

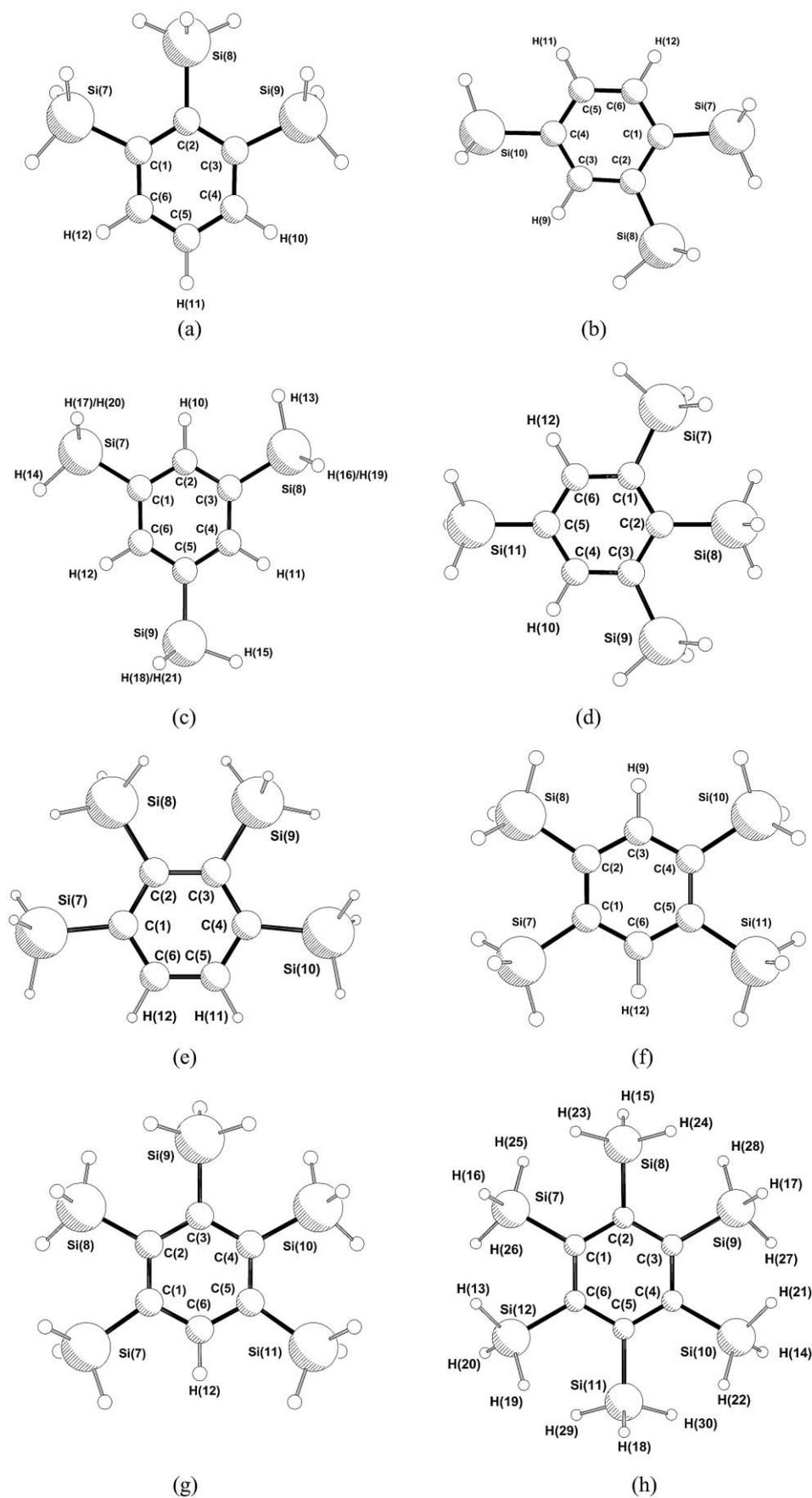


Fig. 1 Computed structures and numbering schemes for (a) 1,2,3-trisilylbenzene, (b) 1,2,4-trisilylbenzene, (c) 1,3,5-trisilylbenzene, (d) 1,2,3,5-tetrasilylbenzene, (e) 1,2,3,4-tetrasilylbenzene, (f) 1,2,4,5-tetrasilylbenzene, (g) pentasilylbenzene and (h) hexasilylbenzene.

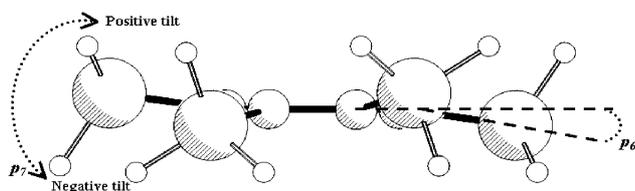


Fig. 2 Diagrammatic representation of the out-of-plane silyl bend parameter, p_6 , and silyl tilt parameter, p_7 . Note the directions of positive and negative tilts.

overestimated the bond lengths, in particular those involving carbon and silicon. This is an artefact of the calculation at this level of theory and is common for bonds between second and third row elements.

The most significant parameters at the highest level of theory are given in Table 2, and complete lists of parameters at all levels are provided in Table S1 (see ESI[†]). Angles defining distortions of C–Si and C–H bonds from planarity at their carbon atoms are

given in full in Table S2 (see ESI[†]), and summarised in Table 3. Computed atomic coordinates and energies are listed in Table S3 (see ESI[†]).

GED refinement

The r_a structure of 1,3,5-trisilylbenzene was refined with both static and dynamic models using the SARACEN method. Experimental data were supplemented by *ab initio* data obtained at the MP2 level of theory using the 6-31G* basis set, with uncertainties based on the variations in the parameters over calculations at different levels. Restraints are listed in Tables 4 and 5, which also give refined geometrical parameters, interatomic distances and amplitudes of vibration. In total eight restraints were placed on parameters and amplitudes of vibration (including ratios of values) that otherwise would not refine satisfactorily. All structural parameters and significant amplitudes of vibration were then included in the refinement, which converged at $R_G = 8.9\%$ (static) and $R_G = 8.8\%$ (dynamic).

Table 2 Computed parameters for the tri-, tetra-, penta- and hexasilylbenzenes^a

Substituent positions	Parameter	MP2/6-31G*	Substituent positions	Parameter	MP2/6-31G*
1,2,3	C(1)–Si(7)	189.0	1,2,3,5	C(6)–C(1)–C(2)	119.0
	C(2)–Si(8)	189.1		C(5)–C(6)–C(1)	121.3
	C(1)–C(2)	142.5		C(4)–C(5)–C(6)	119.6
	C(1)–C(6)	141.0		Si(7)–C(1)–C(2)	124.6
	C(5)–C(6)	139.7		Si(7)–C(1)–C(6)	116.4
	Si(8)–C(2)–C(1)	120.1		C(3)–C(4)–C(5)	118.6
1,2,4	C(2)–Si(8)	188.9	C(4)–C(5)–C(6)	121.2	
	C(1)–Si(7)	188.6	Si(7)–C(1)–C(2)	125.6	
	C(4)–Si(10)	188.0	Si(7)–C(1)–C(6)	115.8	
	C(1)–C(2)	142.3	Si(8)–C(2)–C(3)	120.8	
	C(2)–C(3)	141.1	Si(8)–C(2)–C(1)	119.0	
	C(3)–C(4)	140.9			
	C(4)–C(5)	140.6			
	C(5)–C(6)	139.9			
	C(6)–C(1)	140.9			
	C(1)–C(2)–C(3)	118.6			
	C(2)–C(3)–C(4)	122.9			
	C(3)–C(4)–C(5)	117.6			
	C(4)–C(5)–C(6)	120.6			
	C(5)–C(6)–C(1)	121.8			
C(6)–C(1)–C(2)	118.6				
Si(7)–C(1)–C(2)	125.0				
Si(7)–C(1)–C(6)	116.5				
Si(8)–C(2)–C(3)	117.0				
Si(8)–C(2)–C(1)	124.5				
Si(10)–C(4)–C(5)	121.5				
Si(10)–C(4)–C(3)	121.0				
1,3,5	C(1)–Si(7)	188.0	1,2,4,5	C(1)–Si(7)	188.8
	C(1)–C(2)	141.1		C(2)–C(3)	140.6
	C(2)–C(3)	140.7		C(1)–C(2)	141.7
	C(2)–C(3)–C(4)	118.0		C(1)–C(2)–C(3)	118.5
	C(1)–C(2)–C(3)	122.0		C(2)–C(3)–C(4)	123.0
	Si(7)–C(1)–C(2)	120.9		Si(7)–C(1)–C(2)	123.7
Si(7)–C(1)–C(6)	121.2	Si(7)–C(1)–C(6)	117.8		
1,2,3,4	C(1)–Si(7)	189.4	1,2,3,4,5	C(1)–Si(7)	189.5
	C(2)–Si(8)	189.8		C(2)–Si(8)	189.9
	C(1)–C(2)	142.2		C(3)–Si(9)	190.2
	C(2)–C(3)	142.3		C(1)–C(2)	141.9
	C(1)–C(6)	140.4		C(2)–C(3)	142.3
	C(5)–C(6)	139.3		C(1)–C(6)	140.4
	C(1)–C(2)–C(3)	120.1	C(1)–C(2)–C(3)	119.7	
	Si(7)–C(1)–C(2)	125.6	C(2)–C(3)–C(4)	120.5	
	Si(7)–C(1)–C(6)	115.9	C(5)–C(6)–C(1)	122.9	
	Si(8)–C(2)–C(1)	118.9	C(6)–C(1)–C(2)	118.5	
	Si(8)–C(2)–C(3)	121.3	C(1)–C(2)–C(3)	119.7	
C(1)–C(2)–C(3)	119.7	Si(9)–C(3)–C(2)	119.6		
1,2,3,4,5,6			1,2,3,4,5,6	C–Si	190.5
				C–C	142.0
				C(1)–C(2)–C(3)	120.00

^a Distances in pm, angles in degrees.

Table 3 Angles between C–Si or C–H bonds and the planes defined by the adjacent ring C–C bonds, calculated *ab initio* for the tri-, tetra-, penta- and hexa-silylbenzenes^a

Si positions and point group	Carbon atom	MP2/6-31G*
1,2,3 <i>C_s</i>	C(1)	2.1
	C(2)	–2.0
	C(4)	–2.7
	C(5)	0.9
1,2,4 <i>C₁</i>	C(1)	–1.6
	C(2)	0.8
	C(3)	–0.9
	C(4)	1.3
	C(5)	–0.6
1,3,5 <i>C_{3h}</i>	All	0.0
1,2,3,4 <i>C₂</i>	C(1)	–1.4
	C(2)	2.2
	C(5)	–0.7
1,2,3,5 <i>C_s</i>	C(1)	0.6
	C(2)	–0.7
	C(4)	–0.7
	C(5)	0.3
1,2,4,5 <i>C_{2h}</i>	C(1)	1.2
	C(3)	0.4
1,2,3,4,5 <i>C_s</i>	C(1)	2.6
	C(2)	–4.0
	C(3)	3.9
	C(6)	–1.3
1,2,3,4,5,6 <i>D_{3d}</i>	All	6.6

^a Angles in degrees.

The scattering intensity curves are shown in Fig. S1 (see ESI†) and the radial-distribution curve in Fig. 3. Both models produced virtually identical curves, so only the curves from the dynamic model are shown. The radial-distribution curve contains major peaks at 147.5 pm (C–C and Si–H), 187.5 pm (Si–C), 242.5 pm [C(1)···C(2) and C(4)···C(5)], 285.0 pm [Si(7)···C(4)], 416.0 pm [Si(7)···C(2)], 467.5 pm [Si(7)···C(5)] and 566.5 pm (Si···Si).

Hexasilylbenzene was refined as an *r_a* structure in a similar manner. Seven restraints were placed on parameters and amplitudes of vibration that would not refine on their own, but then all structural parameters and significant amplitudes of vibration were refined, as shown in Tables 6 and 7. The calculation finally converged with *R_G* 8.9%.

The scattering intensity curves are shown in Fig. S2 (see ESI†) and the radial distribution curve in Fig. 4. The radial-distribution curve has major peaks at 145 pm (C–C and Si–H), 190 pm (Si–C), 246 pm [C(1)···C(3)], 287.5 pm [Si(7)···C(2)], 334.5 pm [Si(7)···Si(8)], 419.5 pm [Si(7)···C(3)], 472 pm [Si(7)···C(4)], 569.8 pm [Si(7)···Si(9)] and 660.7 pm [Si(7)···Si(10)].

Table 4 GED structural parameters^a (*r_a*) for 1,3,5-trisilylbenzene

Parameter	Description	Static model	Dynamic model	MP2/6-31G* ^b
<i>p</i> ₁	C–C/Si–H (mean)	144.0(3)	145.0(3)	144.5
<i>p</i> ₂	C–C/Si–H (difference)	9.9(6)	9.9(6)	7.4
<i>p</i> ₃	Si–C	187.3(2)	187.2(2)	188.0
<i>p</i> ₄	C–H	109.3(8)	109.4(8)	109.5(10)
<i>p</i> ₅	C(6)–C(1)–C(2)	119.4(3)	119.4(3)	118.0
<i>p</i> ₆	C–Si–H	108.4(8)	108.4(8)	109.8(10)
<i>p</i> ₇	τ(silyl group)	20.1(59)	n/a	0.0

^a Distances in pm, angles in °. For definitions of parameters, see text. Values in parentheses are the estimated standard deviations. ^b Values in parentheses are the uncertainties used when a computed value was used as a SARACEN restraint.**Table 5** Interatomic distances (*r_a*) and amplitudes of vibration (*u*) for 1,3,5-trisilylbenzene (dynamic model)^{a,b}

Number	Atoms	Distance	Amplitude	Restraint
<i>d</i> ₁	H(10)–C(2)	109.4	7.6	
<i>d</i> ₂	C(2)–C(3)	140.0	3.5(3)	
<i>d</i> ₃	H(13)–Si(8)	149.9	6.3(6)	<i>u</i> ₃ /0.530(25)
<i>d</i> ₄	Si(7)–C(5)	187.3	4.8(3)	
<i>d</i> ₅	H(10)···C(3)	216.2	10.1(9)	9.6(10)
<i>d</i> ₆	C(2)···C(6)	241.8	5.8(4)	
<i>d</i> ₇	C(1)···C(3)	243.2	5.8(4)	<i>u</i> ₆ /1.000(50)
<i>d</i> ₈	H(13)···H(19)	246.3	14.5	
<i>d</i> ₉	H(13)···H(10)	267.2	26.2	
<i>d</i> ₁₀	H(13)···C(3)	274.4	14.9(9)	<i>u</i> ₁₁ /0.470(25)
<i>d</i> ₁₁	C(2)···C(5)	280.0	6.9(3)	<i>u</i> ₁₂ /1.280(50)
<i>d</i> ₁₂	Si(8)···C(2)	284.8	8.6(2)	
<i>d</i> ₁₃	H(16)···H(11)	288.8	23.6	
<i>d</i> ₁₄	H(10)···Si(8)	296.2	16.5(9)	<i>u</i> ₁₂ /0.520(25)
<i>d</i> ₁₅	H(31)···C(4)	307.1	17.9	
<i>d</i> ₁₆	H(13)···C(2)	308.9	19.6	
<i>d</i> ₁₇	H(16)···C(6)	319.7	17.9	
<i>d</i> ₁₈	H(10)···C(6)	340.9	9.3	
<i>d</i> ₁₉	H(19)···H(11)	342.7	23.6	
<i>d</i> ₂₀	H(19)···C(4)	348.2	17.9	
<i>d</i> ₂₁	H(19)···C(2)	367.1	13.9	
<i>d</i> ₂₂	H(19)···H(10)	376.2	18.4	
<i>d</i> ₂₃	H(10)···C(5)	389.3	9.3	
<i>d</i> ₂₄	H(16)···C(2)	392.2	13.9	
<i>d</i> ₂₅	H(13)···C(4)	400.7	12.2	
<i>d</i> ₂₆	Si(8)···C(1)	416.0	9.3(3)	
<i>d</i> ₂₇	H(16)···H(10)	419.0	18.4	
<i>d</i> ₂₈	H(12)···H(10)	431.2	12.6	
<i>d</i> ₂₉	H(13)···H(11)	433.1	16.5	
<i>d</i> ₃₀	H(13)···C(1)	447.7	20.1	
<i>d</i> ₃₁	H(16)···C(5)	455.3	19.5	
<i>d</i> ₃₂	Si(8)···C(6)	467.2	10.3(7)	
<i>d</i> ₃₃	H(19)···C(5)	475.9	19.5	
<i>d</i> ₃₄	H(19)···C(1)	489.9	16.0	
<i>d</i> ₃₅	H(16)···C(1)	509.1	16.0	
<i>d</i> ₃₆	H(13)···C(5)	515.7	13.6	
<i>d</i> ₃₇	H(13)···C(6)	533.9	17.2	
<i>d</i> ₃₈	H(13)···Si(7)	560.9	25.8	
<i>d</i> ₃₉	Si(7)···Si(8)	567.5	13.2(4)	
<i>d</i> ₄₀	H(16)···Si(9)	574.9	24.3	
<i>d</i> ₄₁	H(10)···Si(9)	576.6	10.0	
<i>d</i> ₄₂	H(19)···Si(9)	612.6	24.3	
<i>d</i> ₄₃	H(19)···Si(7)	637.9	18.3	
<i>d</i> ₄₄	H(16)···Si(7)	672.1	18.3	
<i>d</i> ₄₅	H(13)···Si(9)	683.8	13.8	

^a Distances and amplitudes in pm. Values in parentheses are the estimated standard deviations. If no e.s.d. is quoted then the amplitude of vibration was not refined. ^b Long-range H(silyl)···H(silyl) distances were included in the refinement but are not listed here.

Discussion

The effects of silyl substituents on the structures of silyl benzenes are of several distinct, but related, types. First, the silyl group is an electropositive substituent, which leads to narrowing of the ring angle at the carbon atoms bearing the substituents. Secondly, the conformations of silyl groups can have small effects

Table 6 GED structural parameters^a (r_a) for hexasilylbenzene

No.	Description	GED (r_a)	MP2/6-31G ^{*b}
p_1	C–C	142.1(2)	
p_2	Si–C	189.2(2)	
p_3	Si–H	147.0(5)	
p_4	C–C–C	120.0(0)	120.00(2)
p_5	H–Si–H	109.7(6)	108.3(8)
p_6	Silyl group out-of-plane angle	8.9(4)	
p_7	Silyl group tilt	3.2(13)	

^a Distances in pm, angles in °. For definitions of parameters, see text. Values in parentheses are the estimated standard deviations. ^b Values in parentheses are the uncertainties used when a computed value was used as a SARACEN restraint.

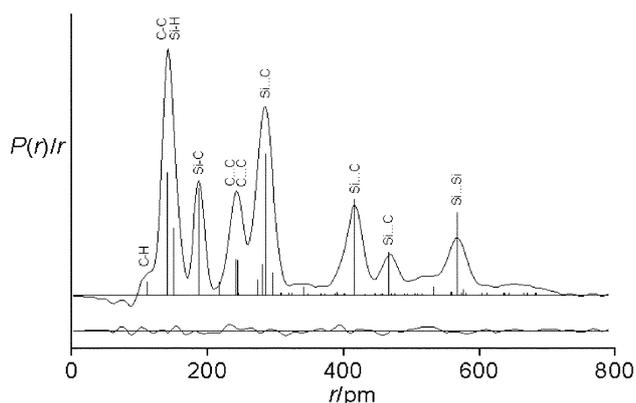


Fig. 3 Observed and final difference radial-distribution curves for 1,3,5-trisilylbenzene. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_{Si} - f_{Si})(Z_C - f_C)$.

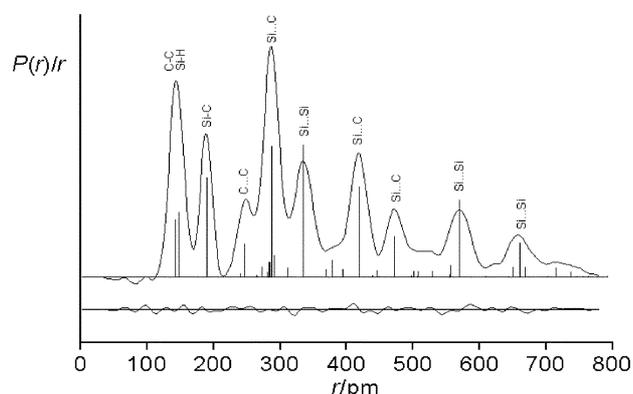


Fig. 4 Observed and final difference radial-distribution curves for hexasilylbenzene. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_{Si} - f_{Si})(Z_C - f_C)$.

on neighbouring bond lengths and angles. Thirdly, interactions between silyl groups on adjacent carbon atoms lead to restriction of their rotation, and then to displacement of C–Si bonds from the ring plane and lengthening of adjacent C–C bonds.

The effects of silyl substituents on the ring angles are small, but consistent with the silyl group being slightly electropositive. The 1,3,5-trisubstituted compound, with its high symmetry, is the ideal compound for studying such ring distortions. The computed CCC angle at the carbon atoms bearing the substituents was computed to be 118.0° (MP2/6-31G^{*}), but the experimental value was significantly larger, at 119.4(3)° for both the static and dynamic models. Experimental angles were also larger than found computationally [MP2/6-311G(d)] for all three disilylbenzenes, with experimental/computed values 119.2(2)/118.8, 119.4(3)/118.0 and 119.0(2)/117.7° for the 1,2-, 1,3- and 1,4-disilylbenzenes respectively.¹ In 1,4-dimethyl-2,5-disilyl-benzene the ring angles at the carbon atoms bearing the

Table 7 Interatomic distances (r_a) and amplitudes of vibration (u) for hexasilylbenzene^a

Number	Atoms	Distance	Amplitude	Restraint
d_1	C(1)–C(6)	142.1	5.3(2)	
d_2	H(13)–Si(12)	147.1	9.3(4)	$u_3/0.539(30)$
d_3	Si(12)–C(6)	189.2	6.0(3)	
d_4	H(19)···H(13)	240.5	15.2	
d_5	C(4)···C(6)	246.0	6.5(6)	
d_6	H(25)···H(23)	265.4	30.9	
d_7	H(13)···C(6)	272.5	13.5	
d_8	H(14)···C(4)	280.6	13.5	
d_9	H(16)···H(13)	280.7	34.3	
d_{10}	C(1)···C(4)	284.1	6.9(4)	$u_{11}/1.200(60)$
d_{11}	Si(12)···C(1)	287.5	8.3(2)	
d_{12}	H(13)···Si(7)	291.9	31.9(18)	$u_{11}/0.264(13)$
d_{13}	H(13)···C(1)	310.6	18.3	
d_{14}	Si(7)···Si(12)	334.5	13.0(3)	
d_{15}	H(14)···C(3)	368.7	18.3	
d_{16}	H(14)···Si(9)	378.9	27.2(26)	29.0(30)
d_{17}	H(13)···C(5)	394.5	18.3	
d_{18}	Si(12)···C(4)	419.5	9.5(3)	
d_{19}	H(25)···H(13)	438.4	38.4	
d_{20}	H(13)···C(2)	445.9	18.6	
d_{21}	H(16)···H(15)	448.2	34.3	
d_{22}	H(13)···Si(11)	471.4	31.6(22)	$u_{23}/0.261(13)$
d_{23}	Si(12)···C(3)	472.0	8.3(5)	
d_{24}	H(18)···H(13)	497.7	34.3	
d_{25}	H(14)···C(6)	501.5	18.6	
d_{26}	H(22)···H(19)	506.3	38.9	
d_{27}	H(13)···C(4)	507.9	18.6	
d_{28}	H(13)···C(3)	529.3	17.8	
d_{29}	H(14)···C(1)	555.7	17.8	
d_{30}	H(13)···Si(8)	556.9	22.6	
d_{31}	Si(10)···Si(12)	569.8	14.0(4)	
d_{32}	H(25)···H(19)	609.7	16.8	
d_{33}	H(15)···H(13)	643.0	38.3	
d_{34}	H(14)···Si(12)	649.5	22.6	
d_{35}	H(21)···H(19)	660.3	35.2	
d_{36}	Si(7)···Si(10)	660.7	13.6(8)	
d_{37}	H(13)···Si(10)	668.7	22.6	
d_{38}	H(15)···H(14)	702.4	38.3	
d_{39}	H(13)···Si(9)	714.6	21.4	
d_{40}	H(14)···Si(7)	737.4	21.4	
d_{41}	H(21)···H(13)	746.8	22.6	
d_{42}	H(25)···H(21)	755.2	28.5	
d_{43}	H(14)···H(13)	763.2	38.3	
d_{44}	H(17)···H(13)	776.8	21.7	
d_{45}	H(25)···H(22)	792.5	23.2	
d_{46}	H(16)···H(14)	833.2	21.7	

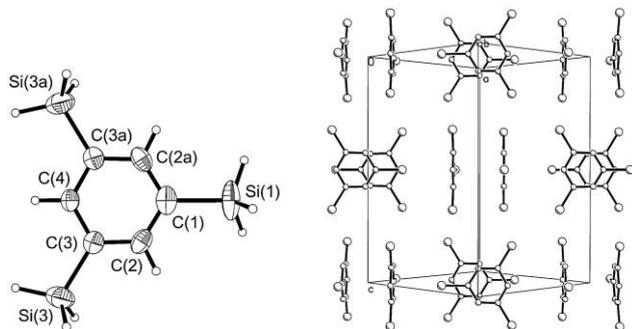
^a Distances and amplitudes in pm. Values in parentheses are the estimated standard deviations. If no e.s.d is quoted then the amplitude is fixed.

silyl substituents are 118.77(13)°.²⁸ Thus silyl groups typically reduce the ring angles by one to two degrees. As phosphorus is only slightly more electropositive than carbon, ring angles adjacent to phosphido groups are typically close to 120°, or up to one degree smaller. Reported values for compounds containing PH₂ groups include 120.1(2) and 119.4(2)° in 1,3-dichloro-5-phosphinobenzene and 120.2(2) and 119.2(2)° in chloro-3,5-diphosphinobenzene.²⁹

For comparison with the gas-phase structure, the structure of 1,3,5-trisilylbenzene was determined in the solid state. The crystal symmetry leads to a molecular point group of C_s rather than one with a three-fold axis. However, this is approximately represented by the parameter values listed in Table 8. In the crystal the molecules of this compound are arranged in pairs, with parallel planes of the benzene rings (see Fig. 5) at a distance of 360.3 pm (compare graphite: 335.4 pm). Compared to the gas phase the CCC angles at the carbon atoms bearing the substituents, C(1) and C(3), are smaller, at 117.4(5) and 117.6(8)°, and thus closer to those calculated *ab initio* (118.0°). The Si–C distances are slightly shorter in the crystal (average 186.4 pm)

Table 8 Structural parameters (distances/pm, angles/°) of 1,3,5-trisilylbenzene as determined by low-temperature X-ray crystallography

Si(1)–C(1)	186.5(6)	Si(1)–C(1)–C(2)	121.3(3)
Si(3)–C(3)	186.3(4)	C(2)–C(1)–C(2a)	117.4(5)
C(1)–C(2)	139.3(5)	C(1)–C(2)–C(3)	122.7(4)
C(2)–C(3)	138.2(5)	C(2)–C(3)–C(4)	117.6(4)
C(3)–C(4)	139.8(5)	Si(3)–C(3)–C(2)	122.7(3)
		Si(3)–C(3)–C(4)	119.7(3)
		C(3)–C(4)–C(3a)	122.0(5)

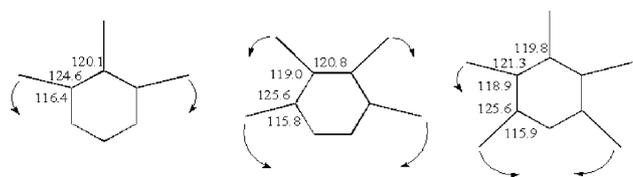
**Fig. 5** Crystal structure of 1,3,5-trisilylbenzene (left) and packing diagram of the molecules showing the unit cell (right). The atoms labelled (a) are those generated by the symmetry operation $x, y, -z + 1$.

than in the gas phase [187.2(2) pm], although the difference lies within three standard deviations for the XRD experiment.

To demonstrate the effects of an extremely electropositive substituent, we calculated the structure of 1,3,5-trilithiobenzene (Table 9). The ring angles at the carbon atoms carrying the lithium substituents are reduced to 114.4°, with the remaining angles therefore 125.6°. The ring bonds are lengthened to 142.3 pm (MP2/6-311+G*) from 139.7 pm in benzene. Unfortunately, data for hexalithiobenzene cannot be obtained, because the lithium atoms shift to positions bridging between carbon atoms.³⁰

The separation of the three silyl substituents in 1,3,5-trisilylbenzene allows the groups almost unrestricted rotation, represented in the GED analysis by use of a dynamic model. Modelling the rotation of the silyl groups makes only a marginal difference to the refinement. This is not surprising, given the small overall contribution of torsion-dependent distances involving these hydrogen atoms to the molecular scattering. However, all the evidence, experimental and theoretical, is that silyl groups that are not adjacent to non-hydrogen substituents in aromatic systems have essentially unrestricted internal rotation. In the compounds with four or more silyl groups, as well as the other isomers of trisilylbenzene, interactions between hydrogen atoms of the silyl groups result in clearly preferred conformations, so that each molecule may have lower symmetry overall than the corresponding trichlorobenzene.

The interactions between silyl groups on adjacent carbon atoms can cause substantial distortions of the molecules. The Si–C–C angles show the effects of increasing steric strain, pushing away from each other wherever possible. These angles can be found in Table 2. The effects are illustrated well by 1,2,3-trisilylbenzene (Fig. 6), for which angles Si(8)–C(2)–C(3) and

**Fig. 6** Si–C–C angles (in °) in the compounds 1,2,3-trisilylbenzene, 1,2,3,4-tetrasilylbenzene, and pentasilylbenzene.

Si(8)–C(2)–C(1) are 120.1°. In contrast, angles Si(7)–C(1)–C(2) and Si(9)–C(3)–C(2) are much larger, at 124.6°, whereas the angles on the other sides of the silyl groups in the 1 and 3 positions are only 116.4°, *i.e.* these groups are pushed outwards by about 4°. Further consequences of these interactions are shown by the tetrasilyl and pentasilylbenzene compounds. In 1,2,3,4-tetrasilylbenzene the silyl groups at the 2 and 3 positions push each other apart slightly (about 1°), while the groups at the 1 and 4 positions are forced even further apart, by 5°. Similar effects are seen in the pentasilylbenzene compound. Fig. 5 shows the Si–C–C angles for the three compounds described above. Modest distortions of this type have been observed previously, in 1,2-disilylbenzene¹ and in 1,4-dimethyl-2,5-disilylbenzene.²⁸ In the latter case the interactions are between methyl and silyl groups, and result in lateral displacement of the silyl groups by just over 1°.

When there are several adjacent silyl groups, the large lateral distortion of the outermost ones is accompanied by displacement out of the ring plane. The out-of-plane angles are listed in Table 3. Where none of the silyl groups are adjacent, as in 1,3,5-trisilylbenzene, the ring and the bonds to it are perfectly co-planar. Two adjacent silyl groups (*e.g.* in 1,2,4-trisilylbenzene) show small displacements, always less than 2°, increasing by about 1° when there are three or four adjacent groups (*e.g.* in 1,2,3-trichlorobenzene). Alternate substituents are always displaced to opposite sides of the ring. The distortions then increase dramatically. In pentasilylbenzene four of the silyl groups are displaced by about 4° from the ring plane, while in hexasilylbenzene the displacement jumps to 6.6° (calculated at the MP2/6-31G* level) or 8.9(4)° (experimental), the latter corresponding to nearly 18° for the SiCCSi dihedral angle. This is close to the value determined by X-ray diffraction for a single crystal of hexasilylbenzene (SiCCSi 15.0°).^{9a} Substantial displacements were also found in hexakis(*p*-tolylsilyl)benzene (7.6°),^{9b} but the effect is observed in its most extreme form in hexakis(trimethylsilyl)benzene, where the SiCCSi dihedral angle is no less than 60.5°.³¹ Moreover, the neighbouring silyl groups in the silylbenzenes tilt (displacing the threefold axis from the Si–C bond) in such a way that the steric interactions with adjacent silyl groups are reduced. The largest tilt for the SiH₃ substituted benzenes was found for hexasilylbenzene, at 3.5(13)°.

Hexa(phosphino)benzene is not known, and the structure of benzene hexathiol has not been determined,³² so one must turn to hexahalobenzenes for other evidence of displacement of substituents from the ring plane. An electron diffraction study of hexachlorobenzene indicated that it was planar, with D_{6h} symmetry,³³ but in the crystalline phase alternate C–Cl bonds are on opposite sides of the ring, although the ClCCl dihedral angles average only a little over 1°.³⁴ For hexabromobenzene

Table 9 Computed parameters for 1,3,5-C₆H₃Li₃ (distances in pm and angles in °) with energies in E_h . Energies are not corrected for ZPE

Parameter	HF/3-21G*	HF/6-31G*	MP2/6-31G*	MP2/6-311G*	MP2/6-311+G*
C–C	141.0	140.8	141.8	142.2	142.3
C–Li	198.7	197.9	200.2	198.3	198.6
C–H	108.4	108.9	109.9	110.0	110.0
C–C(Li)–C	115.4	114.7	115.0	114.4	114.4
C–C(H)–C	124.6	125.3	125.0	125.6	125.6
Energy	–249.7434	–251.1592	–251.9634	–252.0489	–252.0582

the gas-phase data are equivocal, although it is clear that any deviation from planarity is small,³⁵ but in pentabromotoluene the BrCCBr dihedral angles average just over 1°,³⁶ while in hexaiodobenzene the ICCI angles are slightly more than 2°.³⁷ Thus the distortions in hexasilylbenzene are about ten times larger than in the hexahalobenzenes. This would appear to be more than a steric effect. We attribute it to the electron-releasing property of the electropositive substituents, which is associated with increased carbon 2p orbital participation in the neighbouring ring bonds. This normally manifests itself in narrowing of the ring angles, but it should also make it relatively easy for the carbon atom to become pyramidal, and this is most likely to be evident when multiple substitution precludes widening of the ring angles.

The displacement of substituents is not associated with non-planarity of the ring, although such distortion was observed in hexakis(trimethylsilyl)benzene.³¹ Even in hexasilylbenzene, the ring angle refined to 119.98(2)°, which corresponds to a CCCC dihedral angle of about 2(2)°. However, increasing the number of silyl groups does lengthen both C–C and C–Si bonds. The experimental data show that the C–C and Si–C bond lengths in hexasilylbenzene are 2.1 pm and 1.9 pm longer, respectively, than in 1,3,5-trisilylbenzene. Comparing values calculated *ab initio* at the MP2/6-31G* level, it can be seen that the average C–C distance in compounds with three silyl groups is virtually identical to the average with four groups, 141.0 pm compared to 141.1 pm. By the time there are six silyl groups on the ring, the C–C distance has increased by a further 0.9 pm, to 142.0 pm. Interestingly, the calculations show that the two C–C ring distances in 1,3,5-trisilylbenzene differ by 0.4 pm: C(1)–C(2) is found to be longer than C(2)–C(3) (141.1 pm and 140.7 pm, respectively, MP2/6-31G*). This must arise from the orientation of the silyl hydrogen atoms. The shorter C–C distance is for the bond eclipsed by an Si–H bond.

Average computed Si–C bond lengths vary from 188.5 pm (trisilylbenzenes) through 189.2 pm (tetrasilylbenzenes) to 189.8 pm (pentasilylbenzene) and finally to 190.5 pm (hexasilylbenzene). The Si–C bond length is also sensitive to the positions of the substituents relative to one another. For example, in 1,3,5-trisilylbenzene the distance is 188.0 pm, but when one of the silyl groups is moved to a carbon atom adjacent to another silyl group, giving 1,2,4-trisilylbenzene, the average Si–C bond length becomes 188.5 pm. Repeating with the other silyl group, to give 1,2,3-trisilylbenzene, gives a further 0.5 pm increase in the average length. The tetrasilylbenzenes behave similarly: in 1,2,4,5-tetrasilylbenzene the Si–C distance is 188.8 pm, which increases by 0.3 pm in 1,2,3,5-tetrasilylbenzene and by another 0.5 pm in 1,2,3,4-tetrasilylbenzene, where all the substituents are adjacent. It is clear therefore that the Si–C distances reflect steric crowding, but the C–C bond length changes are probably associated with the electropositive nature of the silyl groups.

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