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The molecular structure of triphenylsilane from gas-phase electron diffraction

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Summary

The molecular geometry of gaseous triphenylsilane has been determined by electron diffraction. The silicon bond angles are ideal tetrahedral within experimental error. The benzene rings are slightly elongated in the direction of the Si–C bond. The experimental data are consistent with a C_3 model and a mean torsional angle of 37°, in agreement with published molecular mechanics calculations. The electron diffraction bond lengths (with estimated total errors), among them r_g(Si–C) 1.872(4) Å and r_g(C–C mean) 1.403(3) Å, refer to a well-defined nuclear configuration and differ from the analogous parameters from an X-ray crystallographic study of the same molecule.

Introduction

The molecular structure of gaseous triphenylsilane poses questions in three areas of our interest. These concern the silicon bond configuration [1], the ring deformation in benzene derivatives [1b,2], and the comparison of gas and solid state structures [3]. Allemand and Gerdil [4] determined the crystal molecular structure of triphenylsilane by X-ray diffraction. Párkányi and Hengge [5] reported the results of an X-ray crystallographic study of trimethyltriphenyldisilane which contains the $Si(C_6H_5)_3$ fragment. For the structure of the isolated molecules, full relaxation empirical force field calculations have been performed on triphenylsilane, along with other derivatives, by Mislow et al. [6]. Thus our electron diffraction investigation complements the efforts of other laboratories.

Experimental

Electron diffraction patterns of triphenylsilane were recorded on Kodak electron image plates in a modified [7] EG-100A apparatus at 60 kV accelerating voltage and

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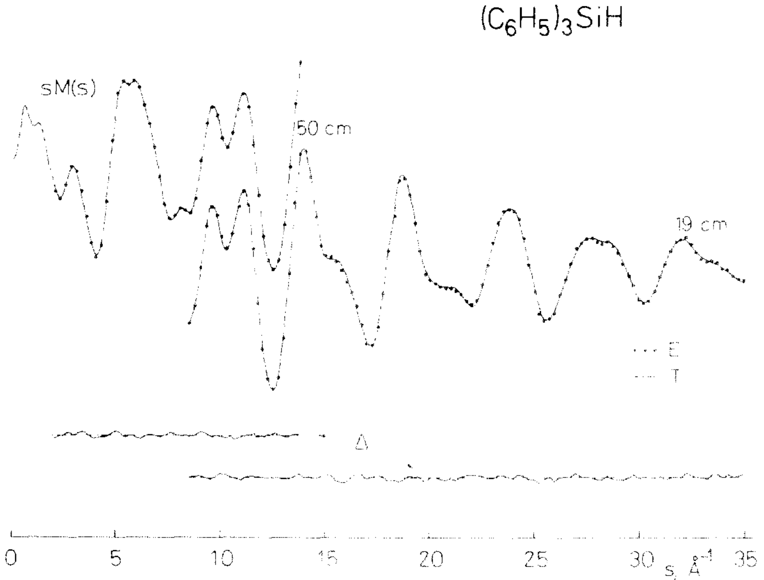

Fig. 1. Molecular intensities: experimental (E) and calculated (T) for the model in Table 1 and the difference curves ($\Delta = E - T$).

at 180 °C nozzle temperature of a stainless steel evaporator. The electron wavelength was obtained from TlCl diffraction patterns [8]. Optical densities of five and four selected plates from the 499 and 191 mm camera distances were transformed

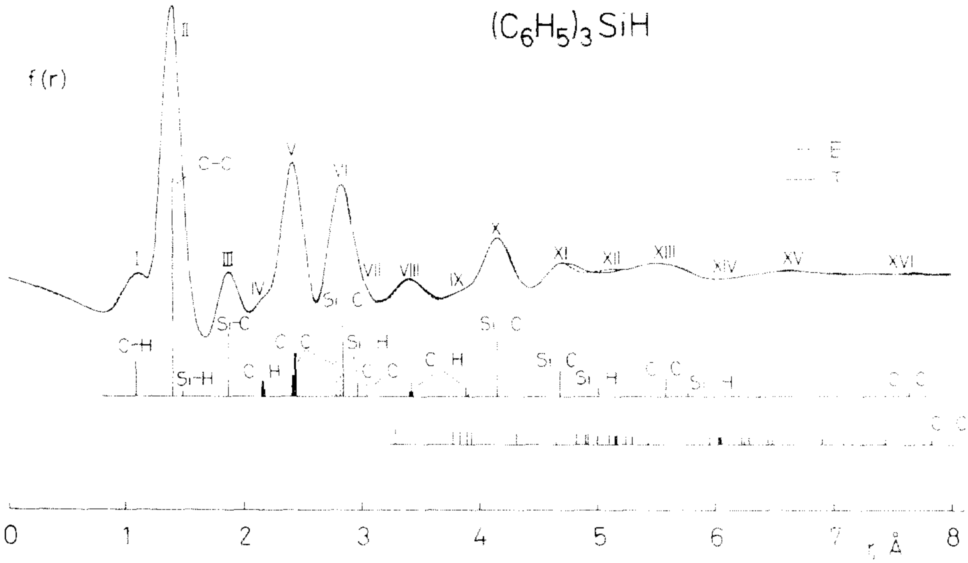

Fig. 2. Radial distributions: experimental (E) and calculated (T) for the model in Table 1, with damping constant a 0.002 $Å^2$. Roman numerals denote the regions for the coupling scheme of amplitudes. Contributions from the rotation-dependent C...C distances are indicated separately.

into electron intensities. (For further details of data reduction and procedures of structure analysis and error estimation see ref. 9.) Reduced molecular intensities (Fig. 1) were used in ranges $2 \leq s \leq 13.75$ with Δs 0.125 Å^{-1} and $8.5 \leq s \leq 35$ with Δs 0.25 Å^{-1} with unit weights. The experimental radial distribution is shown in Fig. 2. The relatively large number of rather well-defined maxima gave promise of a substantial amount of structural information from the electron diffraction data even though this molecule is rather complex for study by this technique.

Structure analysis

The geometry of molecular models (Fig. 3) was defined by the independent parameters listed in Table 1. Local C_{2v} symmetry was assumed for the C_6H_5Si moieties. A mean length was refined for all C–H bonds and it was assumed that the C–H bonds bisect the adjacent CCC angles. The conformation of models was characterized by the angles of rotation of the phenyl groups about the Si–C bonds, τ_1, τ_2 and τ_3, and their signs were defined according to IUPAC recommendations [10]. Thus $\tau_i = 0$ if the corresponding H–Si–C–C sequence is *syn* planar and $\tau_1 = \tau_2 = \tau_3$ if the model has C_3 symmetry (cf. Fig. 3).

Structural parameters were refined by modified versions of a least-squares program [11], using the two ranges of molecular intensities and tabulated values of coherent [12] and incoherent [13] scattering factors.

The experimental radial distribution (Fig. 2) shows distinct peaks for the C–H, C–C and Si–C bond distances. The Si–H bond makes a small contribution, and no attempts were made to refine its parameters. In the range above 3 Å, dispersed contributions from rotation-dependent distances appear, although contributions from rotation-independent distances, viz. C...H within a C_6H_5 group or Si...C, still dominate in the most characteristic peaks (see Fig. 2).

Initial values for the geometrical parameters (r) and vibrational amplitudes (l) were estimated from values in related molecules. Because of the large number of

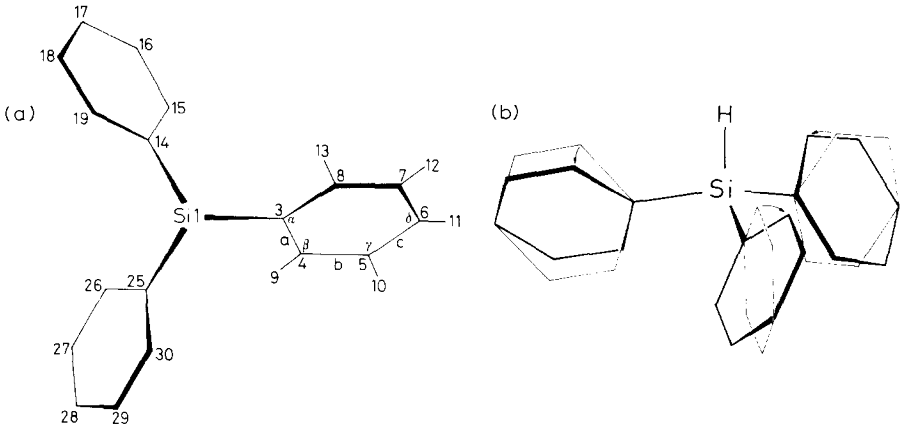

Fig. 3. Molecular models, C_3 symmetry, with numbering of atoms and notation of geometrical parameters. (a) Projection on a plane perpendicular to the Si–H bond. (b) Side view: thin lines indicate the positions of phenyl rings when $\tau_1 = \tau_2 = \tau_3 = 0$.

Table 1

Molecular parameters (r_a, l) of triphenylsilane [a]

Parameter [b]	i	j	r_{ij} (Å; deg)	l_{ij} (Å)	Coupling code for l_{ij}
Independent					
C–H	4	9	1.0943(22)	0.0913(23)	I
C–C	3	4	1.4010(2)	0.0510(4)	II
$b-a$			0 [c]		
$c-b$			0 [c]		
Si–H	1	2	1.4910 [c]	0.0820 [c]	
Si–C	1	3	1.8701(12)	0.0610(12)	III
α			118.87(19)		
γ			120 [c]		
Angle CSiC			109.15(30)		
$\tau_1 = \tau_2 = \tau_3$			36.67(64)		
Dependent					
β			120.76(13)		
δ			119.62(6)		
C...H	3	9	2.162(2)	0.111(3)	IV
	4	10	2.166(2)	0.111(3)	IV
	5	11	2.168(2)	0.111(3)	IV
C...C	4	8	2.413(3)	0.062(1)	V
	5	7	2.422(1)	0.062(1)	V
	4	6	2.427(1)	0.062(1)	V
	3	5	2.436(2)	0.062(1)	V
H...H	9	10	2.489(3)	0.19 [c]	
C...C	5	8	2.794(2)	0.077(1)	VI
	3	6	2.818(3)	0.077(1)	VI
Si...C	1	4	2.850(1)	0.087(1)	VI
Si...H	1	9	2.967(1)	0.157(5)	VII
C...C	3	14	3.048(6)	0.081(5)	VII
	3	15	3.296(9)	0.133(4)	VIII
C...H	8	9	3.406(3)	0.109(4)	VIII
	7	10	3.415(2)	0.109(4)	VIII
	6	9	3.416(2)	0.109(4)	VIII
	4	11	3.420(2)	0.109(4)	VIII
	3	10	3.425(2)	0.109(4)	VIII
C...C	8	14	3.785(6)	0.350(16)	IX
	4	15	3.849(23)	0.410(16)	IX
C...H	7	9	3.888(3)	0.345(16)	IX
C...C	4	14	3.906(13)	0.370(16)	IX
C...H	3	11	3.912(3)	0.345(16)	IX
C...C	8	15	3.949(15)	0.129(2)	X
Si...C	1	5	4.164(1)	0.086(2)	X
C...C	3	19	4.326(5)	0.109(2)	X
	3	16	4.667(9)	0.181(5)	XI
Si...C	1	6	4.688(2)	0.121(5)	XI
C...C	5	15	4.843(22)	0.211(5)	XI
	7	15	4.923(14)	0.348(15)	XII
	8	19	4.937(2)	0.181(5)	XI
Si...H	1	10	5.016(2)	0.308(15)	XII
C...C	7	14	5.025(5)	0.348(15)	XII
	5	14	5.117(13)	0.358(15)	XII

Table 1 (continued)

Parameter [b]	i	j	r_{ij} (Å; deg)	l_{ij} (Å)	Coupling code for l_{ij}
C...C	4	16	5.170(25)	0.408(15)	XII
	8	16	5.178(15)	0.368(15)	XII
	4	19	5.265(11)	0.368(15)	XII
	6	15	5.311(15)	0.227(12)	XIII
	3	18	5.446(6)	0.197(12)	XIII
	3	17	5.588(8)	0.167(12)	XIII
Si...H	1	11	5.782(3)	0.177(12)	XIII
C...C	8	18	5.968(4)	0.436(26)	XIV
	5	16	6.053(26)	0.466(26)	XIV
	7	16	6.060(15)	0.416(26)	XIV
	8	17	6.073(9)	0.386(26)	XIV
	7	19	6.236(3)	0.436(26)	XIV
	4	17	6.262(21)	0.426(26)	XIV
	4	18	6.299(16)	0.436(26)	XIV
	6	16	6.456(17)	0.268(46)	XV
	5	19	6.500(12)	0.258(46)	XV
	6	19	6.920(8)	0.228(46)	XV
	7	17	7.099(10)	0.303(43)	XVI
	7	18	7.172(4)	0.373(43)	XVI
	5	17	7.262(23)	0.353(43)	XVI
	5	18	7.450(17)	0.363(43)	XVI
	6	17	7.640(15)	0.303(43)	XVI
	6	18	7.838(11)	0.333(43)	XVI
R [d]			0.038		

[a] Least-squares standard deviations are parenthesized. [b] See Fig. 3 for notation and numbering of atoms. [c] Assumed value. [d] See ref. 1b.

different distances, the small contributions from the longer H...H distances were neglected in the calculations, while those from rotation-dependent C...H distances were precalculated for each initial model and were assumed to remain unchanged in the refinement cycles. Amplitudes were coupled in various refinements, to form 13 to 17 independent variables altogether, with fixed differences within groups, corresponding to regions of the radial distribution (such regions are indicated by roman numerals in Fig. 2).

First we restricted our models to overall C_3 symmetry, in accord with stereochemical evidence and results of theoretical calculations [6]. As the dihedral angle τ changes, the rotation-dependent distances are thoroughly redistributed and, thus, several local minima were found in the least-squares refinements, initially from 25 to 40° and 50 to 56°. The latter models, however, showed some unreasonably large amplitudes and small CSiC angles as low as 105°.

Among the parameters characterizing the deformation of the phenyl ring (see Fig. 3 and Table 1), c–b and γ are very sensitive to conditions of refinements and b–a often just showed the opposite sign to that expected for a substituent with a silicon atom and so they were restricted to assumed values. In order to examine the influence of such assumptions on the other parameters, b–a and α were given different fixed values, and in some cases the distances Si...C(5), Si...C(6) and

C(3)...C(17) were treated as independent parameters. The mean C–C bond length proved to be independent of such changes, and r(Si–C) varied only within error limits. The assumed conformation of the model had little influence on these parameters.

The CSiC bond angle, on the other hand, depends on the assumptions and is often shifted to low values. Unfortunately, contributions from the C(3)...C(14), C(3)...C(17) and C(6)...C(17) distances, which, together with the Si–C and Si...C(6) distances, would be crucial in determining that angle, strongly overlap with other, partly rotation-dependent, contributions. Arguments from outside the electron diffraction studies, such as the results of molecular mechanics calculations [6] and X-ray crystallographic studies on related substances (see Discussion) are needed to help in assessing our models with different CSiC angles.

Models with lower symmetry were also examined by setting $\tau_1 \neq \tau_2 = \tau_3$. Six combinations of fixed dihedral angles were selected to refine the rest of the parameters. None of these models could be fitted noticeably better to the experimental data than models with C_3 symmetry, and the other parameters, except for the CSiC angle, did not change significantly. The small but systematic discrepancies between experimental and calculated radial distributions could not be eliminated by use of less symmetric models. It was shown that deviations could be decreased by small background adjustments, which, however, did not influence the values of refined parameters. A model with $\tau_1 = 5°$ and $\tau_2 = \tau_3 = 60°$, which has a conformation very close to that found in crystalline $(C_6H_5)_3SiH$ [4], could not be satisfactorily fitted to the electron diffraction data.

A typical result for refinements with the C_3 models is presented in Table 1 and in the theoretical curves of Figs. 1 and 2.

Discussion

The molecular geometry determined for the title compound contains no unexpected features. The silicon bond angles are not distorted from the ideal tetrahedral within experimental error; in view of the bulk of the phenyl ligands, this suggests that the electron pair repulsions in the silicon valence shell dominate in the determination of this bond configuration rather than the ligand/ligand interactions. The benzene rings are elongated, as for the presence of a silyl substituent, but the deformation is smaller than that in other silyl derivatives [1b].

It is of particular interest to compare the structures of the title compound in the gas (present work) and in the crystal [4]. The gas-phase electron diffraction data could not be well approximated by the asymmetric propeller configuration present in the crystal, and characterized by dihedral angles 3.0, 56.7, and 70.9°. However, the C_3 model with dihedral angles of 37° indicated by the gas-phase study cannot be regarded as having serious discrepancy since the electron diffraction results may suffer from keeping the three dihedral angles equal, and the observed mean angle is, in fact, similar to the mean of the dihedral angles from the crystallographic study. It is, of course the conformational properties that are likely to be most affected by any intermolecular interactions in the crystal. There is, however, a marked difference between the Si–C bond lengths determined by the two methods. Unfortunately, the crystallographic Si–C distances are reported with rather large uncertainties (0.013–0.014 Å), however, their mean, 1.852 Å, is appreciably smaller than the electron diffraction r_g(Si–C) value. One of the origins of differences between gas-phase electron diffraction and X-ray crystallographic results is the different physical meaning of the parameters. While an r_g electron diffraction bond length is an average internuclear distance, the X-ray diffraction bond length is an interatomic distance, referring to the positions of the charge centroids in the electron density map. Accordingly, for example, a benzene ring usually appears from X-ray data to be smaller and the ring to substituent distances longer than would correspond to the nuclear positions, unless corrections for the asphericities of the electron density map are applied [14]. While the mean C–C distance from the crystal study is somewhat smaller (1.391 Å) than the electron diffraction mean r_g(C–C) bond length, the small Si–C length reported for the crystal is especially puzzling. In this connection, it is of interest to consider the crystal molecular structure of trimethyltriphenyldisilane, the X-ray study of which also apparently, omitted asphericity corrections [5]. The geometry of the $Si(C_6H_5)_3$ moiety is characterized by a mean Si–C length 1.886(1) Å and a mean C–C length 1.382 Å. Compared with the r_g values for triphenylsilane, the longer Si–C and shorter C–C bonds from the X-ray study are fully consistent with the different physical meaning of the electron diffraction and X-ray data. Note also that the above mentioned Si–C(phenyl) bonds appear to be longer in the crystal than the Si–C(methyl) bonds, viz. 1.862(2) Å, in the same crystal, contrary to stereochemical expectations, but fully consistent with the above discussion.

The conformational properties determined for gaseous triphenylsilane in the present study, are the most appropriate for comparison with the results of the full relaxation empirical force field calculations by Mislow et al. [6]. The point group C_3 was assumed in those calculations, and the torsional angle was determined to be 32.7°, in reasonable agreement with the electron diffraction results. For completeness, we note that the mean torsional angle determined by electron diffraction may be different from that corresponding to the equilibrium structure, primarily because of the vibrations perpendicular to the direction connecting the various nuclei. Theoretical calculations, by definition, refer to the equilibrium structure, and of course, their accuracies are also subject to various limitations (see Note added in proof).

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* *Note added in proof (July 29th, 1987).* Approximate C_3 symmetry, with τ(mean) about 48°, characterizes the perchlorotriphenylsilane ($(C_6Cl_5)_3SiCl$) molecules in the crystal according to a recent X-ray diffraction study [15]. The benzene rings appear to be somewhat smaller, C–C(mean) 1.386(9) Å, and the ring-to-substituent bonds longer, Si–C(mean) 1.91 Å, than those in free $(C_6H_5)_3SiH$. For an interpretation of at least part of the differences, see our discussion above; however, nonbonded chlorine/chlorine repulsions may also be of importance here. The larger CSiC angle of 114° (mean) and ClSiC smaller angle of 105° (mean) of $(C_6Cl_5)_3SiCl$ as compared with the nearly ideal tetrahedral silicon angles of $(C_6H_5)_3SiH$ are consistent with the change in ligand electronegativity brought about by the H/Cl substitution at silicon.