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Electron-diffraction Study of Gaseous Cyclopentasilane

Z. SMITH,[a] H. M. SEIP,[a] E. HENGGE[b] and G. BAUER[b]

[a] Department of Chemistry, University of Oslo, Oslo 3, Norway and [b] Institut für Anorganische Chemie der Technischen Universität, Graz, Austria

Cyclopentasilane, the first cyclic silicon hydrogen compound to be studied by the electron-diffraction method, was found to have very similar geometry to that of cyclopentane. The ring is puckered, and both models with C_2 and C_s symmetry gave very good agreement with the experimental data. This is consistent with the conclusion of a previous spectral study, namely that cyclopentasilane undergoes pseudorotation. However, from electron-diffraction data alone it cannot be established whether the molecule undergoes dynamic pseudorotation or whether it exists in a single static conformation.

Simple molecular-mechanics calculations yielded virtually no energy difference between C_2 and C_s forms, while the difference between puckered and planar conformations was calculated to be between 1.2 and 2.2 kcal mol^{-1},* depending upon the choice of constants used.

The final structural parameters were $r_a(\mathrm{Si-Si}) = 2.342(3)$ Å $r_a(\mathrm{Si-H}) = 1.496(6)$ Å, $\angle(\mathrm{SiSiSi})_{av} = 104.2°(7)$, $u(\mathrm{Si-Si}) = 0.062(2)$ Å, and $u(\mathrm{Si-H}) = 0.082(7)$ Å. The estimated standard deviations for the distance parameters include corrections for systematic uncertainties.

Cyclopentasilane is the first cyclic silicon-hydrogen compound to have been synthesized [1] and studied by Raman and IR spectroscopy.[2] It was considered desirable to complement the spectroscopic study by the electron-diffraction method and molecular-mechanics calculations in order to obtain a more detailed understanding of the molecular structure, since the molecule is of great importance in understanding silicon chemistry.

EXPERIMENT AND DATA PROCESSING

A sample of cyclopentasilane was synthesized as described previously [1] and placed into an ampoule directly usable in the electron-diffraction apparatus. The diffraction diagrams were recorded with a Balzers' Eldigraph KD-G2 [3,4] on 13 cm × 18 cm Replica 23 Agfa-Gevaert photographic plates at a nozzle temperature of about 80 °C. Four plates exposed at a nozzle-to-plate distance of 500.12 mm and two at 250.12 mm were used in the structural analysis. The electron wavelength determined from zinc oxide diffraction patterns was 0.05845 Å and was adjusted to 0.05851 Å by calibration with the diffraction patterns of gaseous benzene.

The intensity values were recorded while oscillating the plates. The experimental intensities were leveled [5] by using the elastic scattering factors calculated by the partial wave method [6] based upon analytical HF potential for Si-atom [7] and using the best electron density of bonded hydrogen for H.[8] The inelastic scattering factors used were those of Tavard *et al.*[9]

The experimental backgrounds were drawn by hand for each plate, and the average molecular intensities were calculated for each set of plates using a modification function $s/(|f'_{Si}||f'_{Si}|)$.[5] The final background correction of 25 cm data was made on the modified intensities for each plate. The intensities for each plate-set were in the s-range 1.125 to 15.00 Å^{-1} and 4.5 to 29.25 Å^{-1} with increment in s of 0.125 and 0.25 Å^{-1}, respectively (see Fig. 1). The radial distribution function calculated by the Fourier transformation of the composite molecular intensity curve is shown in Fig. 2.

CALCULATION OF MEAN AMPLITUDES OF VIBRATION AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS

A complete normal analysis was performed previously [2] using symmetry coordinates for a planar ring. In the present work some modifications were made to this force field in order to simplify use of Gwinn's program [10] for calcula-

* 1 cal = 4.184 J.

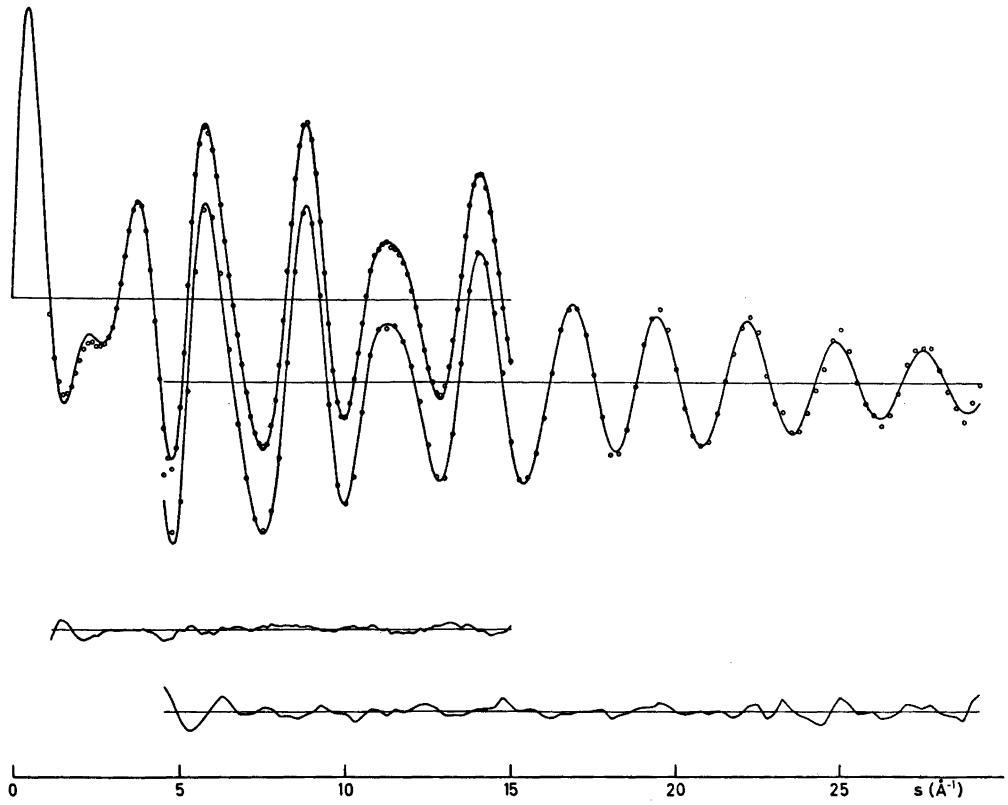

Fig. 1. The experimental intensity data (circles) for cyclopentasilane from the 50 cm ($\Delta s = 0.125$ Å^{-1}) and the 25 cm ($\Delta s = 0.25$ Å^{-1}) nozzle-to-plate distances. The solid line corresponds to the calculated intensities and the lower curves represent the differences between the experimental and calculated intensities. The calculated intensities for models C_2 and C_s are indistinguishable at this scale, therefore only one is shown.

tion of the mean amplitudes of vibration (u^S) and the correction coefficients (K) as described by Stølevik *et al.*[11] Total torsional constants for each Si–Si bond, 0.063 mdyn Å rad^{-2}, were added and two bending force constants were slightly adjusted, namely k_{HSiH} and k_{HSiSi} from 0.54 and 0.52 mdyn Å rad^{-2} to 0.60 and 0.50, respectively, to compensate for the neglection of some coupling constants.

The force field reproduced the observed frequencies sufficiently accurately for calculation of the mean amplitudes of vibration, since they are rather insensitive to moderate changes in the force field. The K-values, however, depend greatly upon the lowest frequency, which was not determined accurately by the experiment;[3] therefore they are less reliable.

The mean amplitudes of vibrations and the correction coefficients were calculated for models C_2 and C_s. Some of the results are given in Tables 1 and 2.

STRUCTURAL ANALYSIS

A comparison of the experimental radial distribution function and the calculated distribution function for a planar (D_{5h} symmetry) model of cyclopentasilane shows the ring to be decidedly nonplanar. The peak corresponding to the Si···Si distance is found at 3.69 Å on the experimental radial distribution function, whereas the expected value for a planar skeleton is about 3.79 Å.

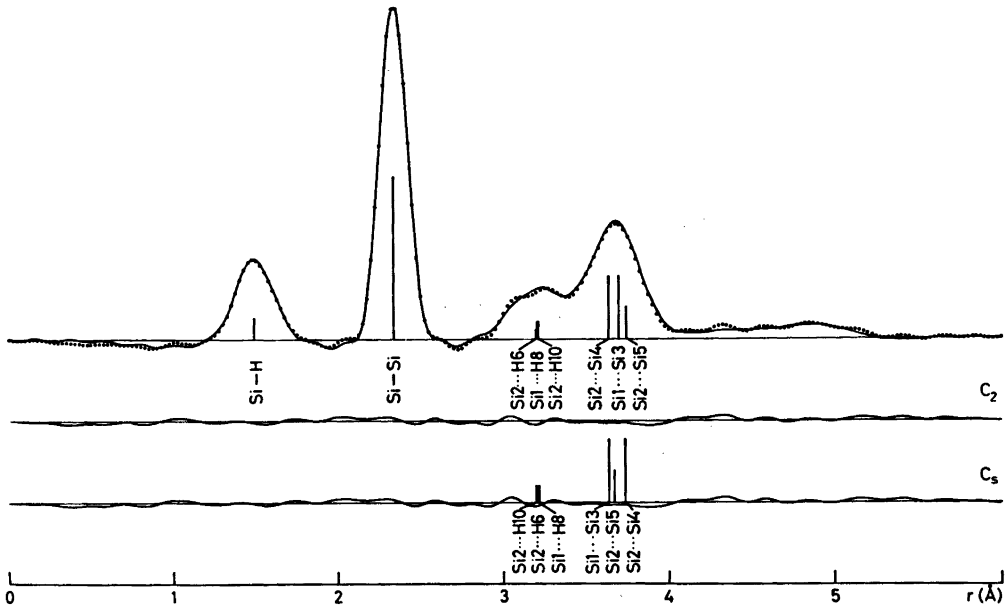

Fig. 2. Experimental (circles) and theoretical (solid line) radial distributions calculated by Fourier transformations of intensity curves composed of the data in Fig. 1. The positions and approximate areas of the most important interatomic distances are indicated for models with C_2 and C_s symmetry. The lower curves represent the difference between the experimental and theoretical curves. Damping constant was 0.0015 Å^2.

Least-squares refinements were carried out for models with C_2 (half-chair) and C_s (envelope) conformations. In both cases the Si–Si bond lengths were assumed equal, as were the Si–H bonds and HSiH angles. The HSiH planes were assumed to bisect the corresponding SiSiSi angles and to be perpendicular to the corresponding SiSiSi plane (for numbering of the atoms see Fig. 3). The constants for the weighting scheme [5,13] are shown in Table 3.

Both C_s and C_2 conformations agree well with the experimental data. The molecular intensities are shown in Fig. 1 and the radial distribution functions in Fig. 2. The theoretical curves are almost identical for the two models; *cf.* the two difference curves given in Fig. 2.

Table 1 shows the final structural parameters determined for Si_5H_{10} when corrections for shrinkage are included. Some non-bonded distances and the corresponding mean amplitudes of vibration for the C_2 model are listed in Table 2. The values of the non-bonded distances correspond to the least-squares refinement with diagonal weight-matrix and corrections for shrinkage (see Table 4, column II) for model C_2. Table 2 should be considered an example of one *possible* instantaneous conformation since only the average Si···Si dis-

Table 1. Structural parameters [a] for Si_5H_{10}.

Parameter	r_a(Å)	u^{ED} (Å)	u^S (Å)	K (Å)
Si–Si	2.342(3)	0.062(2)	0.060	0.008
Si–H	1.496(6)	0.082(7)	0.090	0.027
		Angles (in degrees)		
∠HSiH		105.3(29)		
∠(SiSiSi)$_{av}$		104.3(7)		

[a] For the definition of r_a see Ref. 12. The standard deviations given in parentheses include correction for data correlation [13] and they apply to the last digits given. The deviations for distance parameters are corrected for systematic uncertainties according to $\sigma=[\sigma_{LS}^2+(0.001r)^2]^{\frac{1}{2}}$. The assymmetry constants were (in 10^{-6} Å^3): k (Si–Si)= 2.0 and k (Si–H)= 10.0, zero for non-bonded distances. u^{ED} are mean amplitudes determined by the ED investigation. u^S are mean amplitudes calculated as described in the text for T= 80 °C.

Table 2. Some non-bonded distances and the corresponding mean amplitudes of vibration for the C_2 model.[a]

Parameter [b]	r_a	u^{ED}		u^S	K
Si1···Si3	3.680	0.130	(6)[c]	0.119	0.002
Si2···Si4	3.649	0.131		0.129	0.002
Si2···Si5	3.771	0.124		0.113	0.002
$(Si\cdots Si)_{av}$	3.686				
Si1···H8	3.211[d]	0.151	(8)	0.147	0.023
Si2···H6	3.195	0.151		0.147	0.024
Si2···H10	3.213	0.150		0.146	0.020
Si3···H8	3.210	0.151		0.147	0.022
$(Si\cdots H)_{av}^{short}$	3.208				
Si1···H13	4.303			0.237	0.009
Si2···H13	4.159			0.248	0.010
Si4···H9	4.268			0.248	0.010
$(Si\cdots H)_{va}^{middle}$	4.243				
Si3···H6	4.556			0.222	0.010
Si5···H9	4.649			0.207	0.009
Si3···H7	4.821			0.168	0.010
Si5···H8	4.904			0.174	0.009
Si4···H8	4.938			0.152	0.011
Si1···H12	4.964			0.149	0.009
Si2···H12	4.972			0.150	0.010

[a] The experimental values correspond to the least-squares refinement with diagonal weight-matrix, carried out on a geometrically consistent r_α structure ($r_\alpha = r_a + u^2/r - K$). The distances r_a, amplitudes u, and perpendicular amplitude correction coefficient K are in Å. [b] See Fig. 3 for numbering of the atoms. [c] Parenthesized values are standard deviations from the least-squares refinement in which data correlation is accounted for,[13] and they refer to the last digit given. The indicated parameters were refined in groups. [d] The small difference in the distances Si1···H8 and Si3···H8 originates in the correction for shrinkage of these distances.

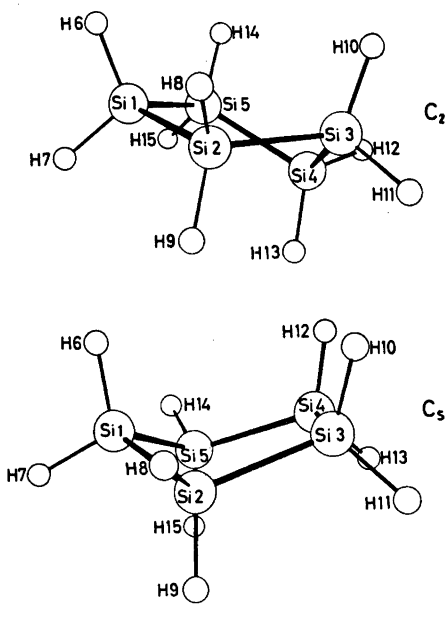

Fig. 3. The C_2 and C_s models of Si_5H_{10}. The numbering of the atoms is indicated.

Table 3. Constants of the weighting scheme.[5,13]

	50 cm	25 cm
s_1 (Å^{-1})	4.5	7.0
s_2 (Å^{-1})	12.5	20.0
w_1	0.12	0.12
w_2	0.05	0.03
P_2	−0.64	−0.60
P_3	0.146	0.125
w	1.0	0.7

tance, $(Si\cdots H)_{av}^{short}$ and $(Si\cdots H)_{av}^{middle}$ can be determined by electron-diffraction. The correlation coefficient between angles Si2Si1Si5 and Si1Si2Si3 is 0.99!

Table 4 shows the most important results obtained in the refinements of the C_2 and C_s models. Again, only the value of the average SiSiSi angle can be relied upon. In fact, the values of ∠Si5Si1Si2 and ∠Si1Si2Si3 can be interchanged (with necessary adjustment of the Si2Si3Si4 angle) and the fit of the data remains the same.

Table 4. Results of various least-squares refinements.[a]

Angle	I C_2	I C_s	II C_2	II C_s
∠Si5Si1Si2	107.7(21)	103.6(19)	104.8(37)	100.5(31)
∠Si1Si2Si3	104.1(15)	102.3(18)	105.7(31)	103.4(27)
∠Si2Si3Si4	102.9(8)	106.6(6)	101.2(9)	105.6(10)
$\angle(SiSiSi)_{av}$	104.3(3)	104.3(2)	103.7(4)	103.7(4)
∠HSiH	105.1(14)	105.4(13)	107.5(12)	107.6(14)
ϕ(Si5Si1 – Si2Si3)	13.3(5)	41.5(9)	14.5(2)	44.1(10)
ϕ(Si1Si2 – Si3Si4)	34.8(11)	25.3(4)	37.7(4)	27.5(8)
ϕ(Si2Si3 – Si4Si5)	43.5(6)	0.0	45.8(18)	0.0

[a] The bond distances were the same in different least-squares refinements within 0.0002 Å. The shrinkage effects were included in calculation I. The parenthesized values are standard deviations from least squares refinements without correction for the correlation between the data. The angles are given in degrees.

Table 5. Conformational energies E (in kcal mol^{-1}) and the corresponding angle parameters calculated by the Westheimer method.[a]

Set	Model	E [b]	E_Θ [b]	E_T [b]	E_V [b]	$(SiSiSi)_{av}$	ϕ_1 [c]	ϕ_2 [c]	ϕ_3 [c]	Angle HSiH
I	C_2	3.86	1.25	3.29	−0.68	105.0	12.1	31.7	39.0	109.9
	C_s	3.86	1.25	3.29	−0.68	105.0	37.2	23.1	0.0	109.9
	D_{5h}	5.07	0.16	5.5	−0.59	108.0	0.0	0.0	0.0	109.1
	$\Delta E = 1.21$ [d]									
II	C_2	3.27	1.26	2.74	−0.73	103.8	14.3	37.3	45.9	110.2
	C_s	3.27	1.26	2.74	−0.73	103.8	43.7	27.2	0.0	110.2
	D_{5h}	5.03	0.12	5.5	−0.59	108.0	0.0	0.0	0.0	109.1
	$\Delta E = 1.76$									
III	C_2	1.93	1.08	2.73	−1.87	103.8	14.3	37.4	46.1	111.0
	C_s	1.93	1.08	2.73	−1.87	103.8	43.9	27.3	0.0	111.0
	D_{5h}	3.94	0.03	5.5	−1.59	108.0	0.0	0.0	0.0	110.0
	$\Delta E = 2.01$									
IV	C_2	1.37	1.03	2.73	−2.39	103.7	14.4	37.4	46.1	112.2
	C_s	1.37	1.03	2.73	−2.39	103.7	43.9	27.3	0.0	112.2
	D_{5h}	3.56	0.00	5.50	−1.94	108.0	0.0	0.0	0.0	111.1
	$\Delta E = 2.19$									

[a] Constants used in all calculations (stretching force constants in mdyn Å^{-1}, bending force constants in mdyn Å rad^{-2}, barrier V^0 and parameter ε in kcal mol^{-1}; natural values are denoted by ^{0}): $r^0_{SiSi} = 2.34$ Å, $r^0_{SiH} = 1.50$ Å, van der Waals radius r^*_{Si} was estimated 1.95 Å by comparing the radii of neighbouring atoms in the periodic table,[16] $\varepsilon_{HH} = 0.042$ (from Ref. 14), ε_{SiH} was assumed to be the same as ε_{SH} which is 0.115 (from Ref. 14), $V^0_{SiSi} = 1.1$ (Ref. 17), $\theta^0_{SiSiH} = 109.4°$, $k_{HSiH} = 0.38$ (Ref. 18), $k_{SiSiH} = 0.46$, the bond stretching constants were $k_{SiH} = 2.72$ and $k_{SiSi} = 1.82$. The values of the following constants were changed in the different sets: k_{SiSiSi} was 0.4 (set I), 0.2 (II), 0.3 (III), 0.35 (IV), θ^0_{SiSiSi} was 109.4 (I and II), 108.0 (III and IV), θ^0_{SiSiSi} was 108.4 (I and II), 109.4 (III), 111.0 (IV), r^*_H was 1.2 (I and II), 1.6 (III) and 1.75 (IV). [b] E is the conformational energy of a single conformation, $E\Theta$ is the sum of bending energies, E_T is the sum of the torsional energies and E_V is the sum of the van der Waals energies (for definitions see Ref. 14). [c] ϕ_1 is a torsional angle ϕ (Si5Si1 – Si2Si3), ϕ_2 is ϕ (Si1Si2 – Si3Si4) and ϕ_3 is ϕ (Si2Si3 – Si4Si5). [d] ΔE is an energy difference between planar conformation and C_2 or C_s conformation.

Because of the uncertainty in the K values, the results obtained both with and without shrinkage correction are presented in columns I and II, respectively.

MOLECULAR-MECHANICS CALCULATION

Simple molecular-mechanics calculations [14] were carried out for models with C_2, C_s and D_{5h} symmetry. The energies of some symmetry-unrestricted models were also calculated, but the geometry always converged close to either the C_2 or C_s model. The difficulty of the calculation in this case lies in the fact that many of the constants needed for the calculation are not available and therefore must be estimated.

The results of some calculations and the constants used are shown in Table 5. The SiH bond distance was assumed 1.50 Å. Assumptions about HSiH angles were the same as before. A computer program [15] calculating energy minima by a combination of the steepest-descent and the Newton-Raphson method was used. It is clear that for any set of constants tried, models with C_2 and C_s symmetry have virtually the same energy. The difference between C_2 or C_s and the planar conformation was estimated to be between 1.2 and 2.2 kcal mol^{-1}.

DISCUSSION

The Si–Si distance in cyclopentasilane, 2.342(3) Å, is appreciably longer than that in disilane,[19] 2.331(3) Å, but in good agreement with the same distance in hexamethyldisilane,[20] 2.340(9) Å. Similar lengthening is observed in cyclopentane,[21] where the C–C bond is 1.546(1) Å, while that in ethane is 1.534(1) Å.[22] The degree of puckering in cyclopentasilane is remarkably similar to that in cyclopentane. The average CCC angle is 104.5° in C_5H_{10} and in Si_5H_{10} the average SiSiSi angle is 104.3°.

An inspection of Fig. 2 shows that although the individual non-bonded distances vary in the two models, the radial distribution function does not. Accordingly, it is not possible to establish by the electron-diffraction method alone whether the molecule undergoes dynamic pseudorotation or whether it exists in a single static conformation. The situation seems to be identical to that of cyclopentane.[21]

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