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1,1,2,2-tetrachlorodisilane (Cl₂HSi–SiHCl₂): molecular structure, conformation and torsional potential as determined by gas-phase electron diffraction, vibrational spectroscopic data and ab initio molecular orbital calculations

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Dedicated to Professor Lawrence S. Bartell on the occasion of his 75th birthday

Abstract

The molecular structure, conformational composition and torsional potential of 1,1,2,2-tetrachlorodisilane (TCDS), Cl₂HSi–SiHCl₂, were studied using gas phase electron diffraction (GED) data at 23°C, together with earlier recorded spectroscopic data and normal coordinate- and ab initio molecular orbital calculations. The title compound exists in the gas phase at room temperature as a mixture of two conformers, *anti*, with a torsion angle $\phi(\text{HSiSiH}) = 180°$, and *gauche*, with a torsion angle $\phi(\text{HSiSiH}) \approx 60°$. The *gauche* conformer predominates, occupying approximately 80% of the gas composition at 23°C. Some structural parameter values obtained from the GED refinements, using results from the earlier spectroscopic work and ab initio molecular orbital calculations as constraints, are as follows (*gauche* conformer with estimated 2σ uncertainties): bond lengths (r_g): $r(\text{Si–Si}) = 2.310(8)$ Å, $r\langle(\text{Si–Cl})\rangle = 2.039(2)$ Å (average value), $r(\text{Si–H}) = 1.511$ Å (assumed value). Bond angles ($\angle\alpha$): $\angle\langle\text{SiSiCl}\rangle = 108.9(4)°$ (average value), $\angle\text{ClSiCl} = 109.7(3)°$, $\angle\text{SiSiH} = 111.5°$ (assumed value). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: 1,1,2,2-tetrachlorodisilane; Conformational structure; Electron diffraction; Torsional potential; Vibrational spectroscopy

1. Introduction

Interests in studying the conformational structures and energy barriers in di- and trisilanes have typically been founded on observing how far the analogy with the corresponding alkane molecules extended. Lately, these interests have turned more towards the intrinsic nature of structural silicon chemistry itself, as more

and more experimental data were published [1]. The experimental information on the silanes and disilanes are important in the structural silicon chemistry knowledge. The geometrical structure of disilane, Si₂H₆, was reported in 1972 [2] and that of the hexachlorodisilane (Si₂Cl₆) determined by gas phase electron diffraction (GED) several times, most recently in 1973 [3].

The amount of structural information published for the substituted disilanes is, however, small compared to the body of knowledge available for the alkanes, though a few halogen-substituted disilanes have been
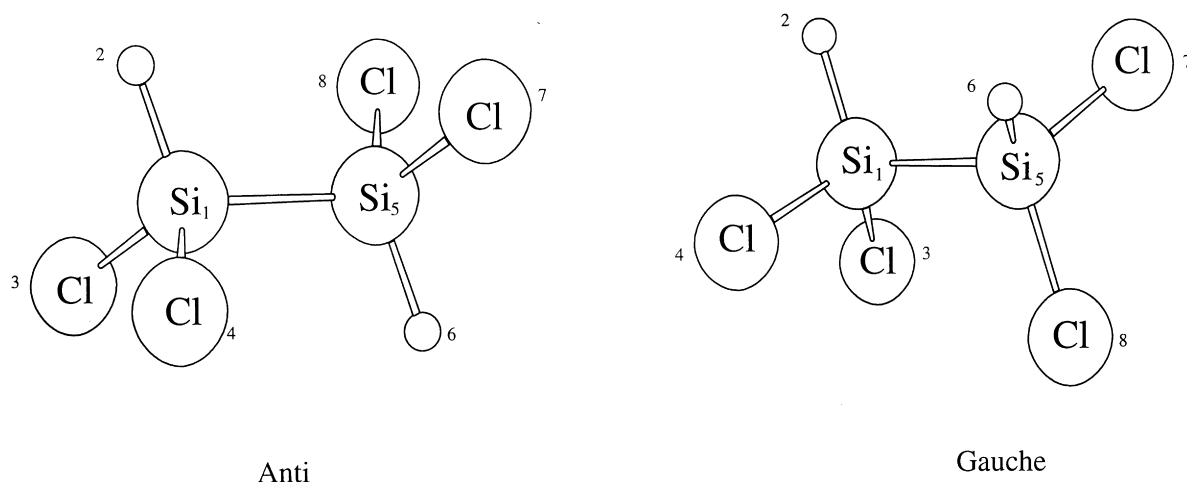
Fig. 1. Molecular models of *anti* and *gauche* conformers of 1,1,2,2-tetrachlorodisilane showing the atom numbering.

experimentally studied [4–16], either by GED, microwave spectroscopy (MW), vibrational infrared (IR) or Raman spectroscopy, or by dipole moment measurements [11–13]. The structural studies published include molecules (studied by GED unless otherwise noted) such as: 1,1,2,2-tetrabromo-disilane (Br_2HSi–$SiHBr_2$) [4], 1,1,2,2-tetraiododisi-lane, and 1,2-diiododisilane (I_2HSi–$SiHI_2$ and IH_2Si–SiH_2I) [5], 1,1,1-trifluorodisilane (H_3Si–SiF_3, MW) [6], fluorodisilane (FH_2Si–SiH_3, MW) [7], hexafluorodisilane (F_3Si–SiF_3) [8,9], iododisilane (IH_2Si–SiH_3, MW) [10] and 1,2-dichlorotetramethyl-disilane (Me_2ClSi–$SiClMe_2$; Me = CH_3) [14]. Vibra-tional studies of Br_2HSi–$SiHBr_2$ [15], I_2HSi–$SiHI_2$ [15] and of 1,1,2,2-tetrachlorodimethyl-disilane ($MeCl_2Si$–$SiCl_2Me$) [16] have also been reported.

In all cases where rotational isomerism is possible, two conformers were observed, the *anti* and *gauche* forms. In many cases, a determination of the confor-mational composition, and thereby the conformer energy differences, were also performed and these results were reviewed in a recent article [16].

The molecular structure of 1,1,2,2-tetrachlorodisi-lane (Cl_2HSi–$SiHCl_2$; TCDS, Fig. 1), was not previously determined experimentally, but the mole-cular mechanics calculations (MM) were made [17], and the IR/Raman spectra recorded and analyzed [18], for both TCDS and its d_2-isotopomer, Cl_2DSi–$SiDCl_2$. The spectra clearly showed the simultaneous existence of both an *anti* (H–Si–Si–H torsion

angle $\phi = 180°$) and a *gauche* (H–Si–Si–H torsion angle $\phi \approx 60°$) conformer in both the gas and liquid phases. The energy difference between the confor-mers was determined to be 0.45 ± 0.17 kcal mol^{-1} from the temperature dependent FT-Raman spectra in both the pure liquid and benzene solutions, with the *gauche* conformer being the more stable one. The magnitude of this energy difference is such that it should be possible to detect the *anti* form by GED studies.

In the MM-calculations [17], the *gauche* form of TCDS was found to be more stable than the *anti* form by 0.7 kcal mol^{-1}. Ab initio molecular orbital calcu-lations have also been reported [18]. Using HF/SBK-ECP pseudo-potentials, the *anti* form was calculated to be lower in energy than the *gauche* form by 0.50 kcal mol^{-1}. This result contradicts both the experimental Raman and the MM results. For Br_2HSi–$SiHBr_2$ [4], the GED investigation found the *anti* conformer to be more stable than the *gauche* form by 0.5 ± 0.6 kcal mol^{-1}, while the analogous tetraiododisilane [5] also had the *anti* form lower in energy (by 0.2 ± 0.6 kcal mol^{-1}). However, for the disubstituted compound, IH_2Si–SiH_2I [5], the *gauche* form was found to be more stable by 0.3 ± 0.6 kcal mol^{-1}. For $MeCl_2Si$–$SiCl_2Me$ [16], an energy difference of 0.25 ± 0.05 kcal mol^{-1} between the conformers was determined from variable temperature Raman spectra in the liquid state, with the *anti* form being more stable (average value of
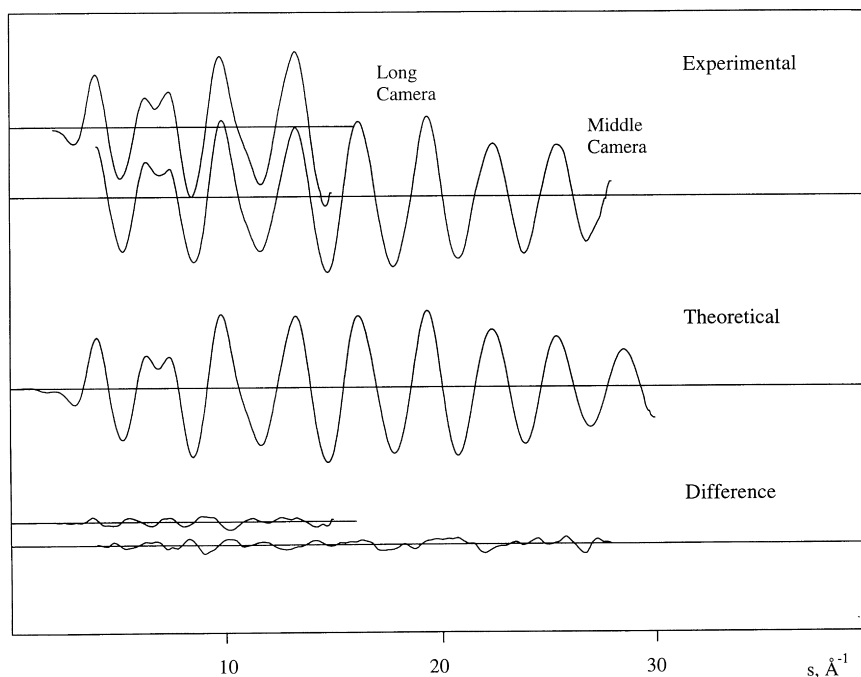
Fig. 2. Intensity curves ($sI_m(s)$) for 1,1,2,2-tetrachlorodisilane. The experimental curves are averages of six plates each from the two camera distances. The theoretical curve was calculated from the structural parameters given in Table 1. The difference curves result from subtracting the relevant part of the theoretical curve from the experimental curves.

two isotopomers, h_6 and d_6). Thus, if the Raman value for TCDS is correct, it implies that substituting the two hydrogen atoms in TCDS with methyl groups has a substantial effect on the conformer energies. For the similar $Me_2ClSi–SiClMe_2$, it was observed [14] that the *gauche* conformer was more stable at 40°C, with the obtained energy difference being $0.6 \pm 0.5 \, kcal \, mol^{-1}$.

The overall range of the conformational energy differences in the disilanes discussed is 0–2.4 kcal mol^{-1} [16]. Clearly, it is of interest to see how the TCDS value compares with these values. It is also of interest to see if the discrepancy between the ab initio energy difference value and the published experimental value [18], can be resolved or explained. It was hoped that a combined GED/ab initio investigation of TCDS would provide experimental results that could resolve the controversies regarding conformer stability, and possibly also provide some further evidence on the importance of the ''*gauche*-effect'' [19], in relation to conformer stability in these

types of molecules. In addition, our study should provide a reliable experimental molecular structure for TCDS and possibly give information about the structure dependence of disilanes upon substitution by different halogens.

2. Experimental section

The sample of TCDS was obtained [18] from Karl Hassler, Institut für Anorganische Chemie, Technische Universität Graz, Austria. Electron-diffraction patterns were recorded with the Balzers Eldigraph KD-G2 (40 kV) at the University of Oslo [20] on Kodak Electron Image plates with a nozzle-tip temperature of 296 K. Nozzle-to-plate distances were 498.82 and 248.77 mm for the long camera (LC) and the middle camera (MC) distance experiments, respectively. The electron wavelength was $\lambda = 0.058625$ Å. Six diffraction photographs from each of the two camera distances were used in the
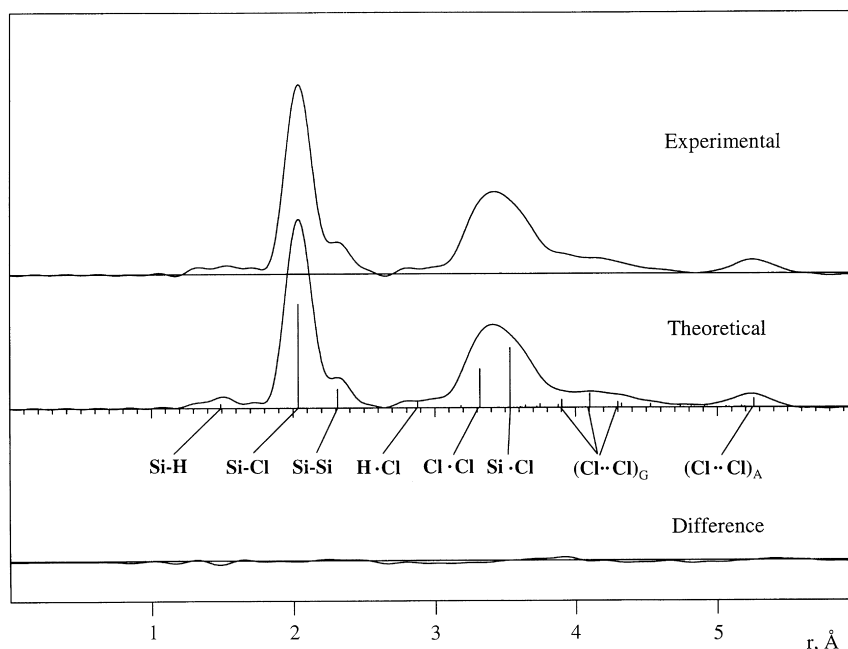
Fig. 3. Radial distribution curves for 1,1,2,2-tetrachlorodisilane. The experimental curve was calculated from the composite of the two average experimental curves shown in Fig. 2 with the use of theoretical data for the region $0 \le s/\text{Å}^{-1} \le 1.75$ and $B/\text{Å}^2 = 0.0020$. The difference curve is experimental minus theoretical. The vertical lines indicate the interatomic distances, they have lengths proportional to the distance weights.

analysis. A voltage/distance calibration was made with benzene as reference ($r_a(\text{C}=\text{C}) = 1.3975$ Å) [21]. Optical densities were measured using an Agfa ARCUS II commercial scanner [22] at the University of Oslo, and the data were reduced in the usual way [23–25]. The ranges of data were $2.00 \le s/\text{Å}^{-1} \le 15.00$ and $4.00 \le s/\text{Å}^{-1} \le 28.00$ for the LC and the MC distance experiments, respectively. The data interval was $\Delta s = 0.25$ Å^{-1}.

A calculated background [26] was subtracted from the data for each plate, to yield experimental intensity curves in the form $sI_m(s)$. The average experimental intensity curves are shown in Fig. 2. Fig. 3 shows the final experimental radial distri- bution (RD) curve calculated in the usual way from the modified mole- cular intensity curve $I'(s) = sI_m(s)Z_{Si}Z_{Cl}(A_{Si}A_{Cl})^{-1} \exp(-0.002s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes. Theoretical intensity data were used for $s \le 1.75$ Å^{-1} in the experimental curve before the RD curve was calculated. The

scattering amplitudes and phases were taken from tables [27].

3. Structure analysis

3.1. Details of the dynamic model

The GED data were treated by using a dynamic theoretical model. This involved fitting a chosen two-term cosine potential function to the experi- mental data. This made it possible to obtain an experi- mentally refined value for a threefold potential constant (V_3) in the series $V(\phi) = 1/2\Sigma_i \times V_i[1 - \cos i(180 - (\phi)]$, with $i = 3$, where ϕ is the value of the torsional angle HSiSiH. Also the V_1 term was included, but as both the potential constants could not be refined simultaneously, this parameter was set as a constant so as to give *gauche* the relative energy obtained from the IR/Raman work [18]. The cosine potential [28] was obtained by

Table 1
Structural parameters for 1,1,2,2-tetrachlorodisilane[a]

	Electron diffraction				Ab initio[b]	
	$r_\alpha/\angle_\alpha$ anti	r_g anti	$r_\alpha/\angle_\alpha$ gauche	r_g gauche	$r_e/\angle$ anti	$r_e/\angle$ gauche
$r(Si–Si)$	2.305(8)	2.309	2.307(8)	2.310	2.336	2.337
$r(\langle Si–Cl\rangle)$	2.033(2)	2.042	2.031(2)	2.039	2.052	2.050
$r(Si–H)$	[1.496]	[1.510]	[1.497]	[1.511]	1.479	1.480
$\angle SiSiCl\rangle$	108.2(4)		108.9(4)		108.5	108.7
$\angle SiSiH$	[112.8]		[111.5]		112.8	112.5
$P(ClSiCl)$	118.8(7)		119.6(7)			
V_1 (kcal mol^{-1})[c]	$-0.6(\pm 0.2)$[d]					
V_3 (kcal mol^{-1})[c]	1.5 ± 0.5					
ϕ (torsional angle)	[180]		[60]		180.0	66.2
α ($\times 100$)[e]	20		80		44.2	55.8
$\Delta E_{G–A}$ (kcal mol^{-1})		-0.45			$+0.27$	
Dependent parameters	$r_\alpha/\angle_\alpha$	r_g	$r_\alpha/\angle_\alpha$	r_g	$r_e/\angle$	$r_e\angle$
$r(Si–Cl_{3,8})$	2.033(2)	2.042	2.027(2)	2.036	2.052	2.047
$r(Si–Cl_{4,7})$	2.033(2)	2.042	2.034(2)	2.043	2.052	2.053
$\angle SiSiCl_{3,8}$	108.2(4)		110.0(4)		108.5	109.3
$\angle SiSiCl_{4,7}$	108.2(4)		107.9(4)		108.5	108.2
$\angle ClSiCl$	109.7(3)		109.7(3)		110.0	110.5
$\angle HSiCl$	108.9(5)		108.9(5)		108.5	108.2

[a] Distances (r) are in ångstroms (Å), angles ($\angle$) in degrees. Parenthesized values are 2σ, where σ include estimates of uncertainty in voltage/nozzle heights and of correlation in the experimental data.

[b] MP2/6-31G(d) calculations: the constraints used in the parameters between the conformers are HF/6-31G(d) values.

[c] The refined potential constants obtained from the dynamic model; see the text.

[d] Based on the experimental energy value from Ref. [18].

[e] Estimated mole fractions of the conformers in percent. In both cases Boltzmann statistics were utilized.

using pseudo-conformers, each one being a representative of a finite displacement of the large-amplitude torsional coordinate, and each giving a weight determined by Boltzmann statistics in which the cosine potential $V(\phi)$ appeared as the energy factor.

The cosine potential function $V(\phi)$ has the property that $V(180°) = 0$, $V(0°) = V_1 + V_3$, and $V(60°) = 3/4 V_1$. The FT-Raman energy difference value of -0.45 kcal mol^{-1} indicated that $V_1 = -0.6$ kcal mol^{-1}, which was utilized in the final refinement. By using pseudo-conformers at 15° intervals from *syn* (0°) to *anti* (180°), comprising a total of 13 pseudo-conformers, a refined value for V_3 was obtained, and from these values for V_1 and V_3 the experimental torsional potential curve for the rotation around the Si–Si bond could be calculated. The C_{2h} forms (0° and 180°) were given half the statistical weight of the C_2 forms (15° through 165°) in the Boltzmann calculations because of

multiplicity considerations. Attempts at refining the constants V_2, V_4 and V_6 (mentioned later) were not successful and these constants were therefore set to zero.

3.2. Ab initio molecular orbital calculations

Ab initio molecular orbital calculations were used to establish constraints in our dynamic GED model by incorporating calculated geometrical differences between the different forms as constants. The geometries for both stable conformers of TCDS were fully optimized at the MP2/6-31G(d) level using GAUSSIAN 94 [29]. Geometry optimizations were also performed at the HF/6-31G(d) level for each pseudo-form at 30° intervals, and these results were used as constraints in the refinement. It was also found necessary to perform higher-level calculations, utilizing MP4(SDQ-fc)/6-31 + + G(d,p) level of theory, which had diffuse and polarization functions
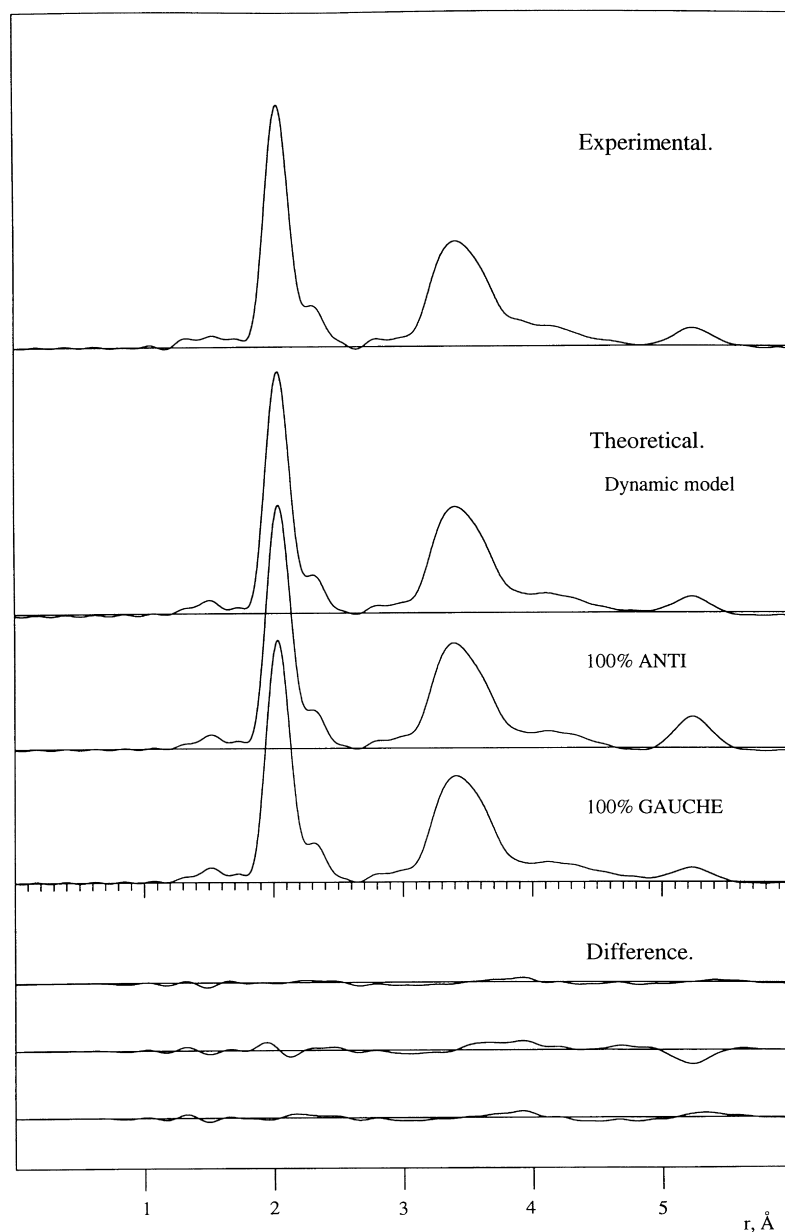
Fig. 4. Theoretical radial distribution curves for 1,1,2,2-tetrachlorodisilane, showing the final theoretical model as obtained from the refined potential curve in the dynamic model (theoretical), and theoretical 100% curves for each minimum conformer ''*anti*'' and ''*gauche*'', as labeled, together with the experimental curve (experimental) and difference curves (difference).

on all atoms, and used the frozen core (fc) approximation. The purpose of the MP4(SDQ-fc) calculation was to see if a higher level of ab initio theory could improve the discovered discrepancies regarding the conformational energy differences. The procedure of

using ab initio results as constraints in the GED analysis has been shown to be very useful [30–32].

Zero-point energies (ZPE) were also estimated at the MP2 ab initio optimized geometries. Energy estimates obtained for the conformers at the MP2/6-

31G(d) level were used to calculate a theoretical conformational composition by using simple Boltzmann statistics. These values, along with the experimental geometrical parameters and the refined potential constant obtained from the GED analysis, are shown in Table 1. The ab initio HF/6-31G(d) level of theory was used to calculate a torsional potential curve for rotation around the Si–Si bond by using the SPARTAN IBM Release 4.1.1 software package [33]. This torsional potential curve is shown in Fig. 5, together with the potential curve obtained by plotting the experimentally obtained energy values shown in Table 4.

3.3. Refinements, vibrational corrections and normal coordinate calculations

From the experimental RD curve and from the results obtained for related molecules, as well as from the results from theoretical calculations, trial values for bond distances and bond angles were obtained for TCDS. Refinements of the molecular structure based on the GED data were made by the least-squares method [34], adjusting a theoretical $sI_m(s)$ curve simultaneously to the 12 experimental intensity curves, one from each of the photographic plates, using a unit weight matrix. The structures were converted from the geometrically consistent r_α to the r_a-type, required by the formula for the theoretically scattered intensities ($r_a = r_g - l^2/r = r_\alpha - l^2/r + K_T + \delta r$) [35,36], by using the values of the centrifugal distortion constants (δr), perpendicular amplitude corrections (K_T) and root-mean-square amplitudes of vibration (l) calculated at the temperature of the experiment, 296 K.

These vibrational quantities were estimated from the ab initio Cartesian force fields (HF/6-31G(d)) using normal coordinate calculations (NCA) and the program ASYM4o [37]. The Cartesian force fields were used as input to the program and then transformed into force fields based on non-redundant symmetry coordinates. A set of scale factors for the non-redundant set of symmetry force constants for each conformer was then refined to fit the observed vibrational wavenumbers [18] for two available isotopomers, $H_2Cl_4Si_2$ and $D_2Cl_4Si_2$. The resulting scaled quantum-mechanical (SQM) force fields were used to calculate the quantities described earlier, with addi-

tional corrections made for the removal of the torsional normal mode (mentioned later). The ab initio force field and the NCA calculations assumed C_{2h} symmetry (species A_g, A_u, B_g, B_u) for the *anti* conformer, and C_2 symmetry (species A and B) for the *gauche* conformer. The calculated wavenumbers from the SQM force fields agreed with the experimental ones within an average of ± 8 cm^{-1} margin, which seemed acceptable. The sets of scale constants and force fields are not included here, but may be obtained from the authors upon request.

The use of a dynamic model in the GED analysis enforces removal of the contribution from the large-amplitude torsional symmetry coordinate to the harmonic NCA calculations [28], and the corresponding diagonal internal force constants were therefore set to intentionally high values (*anti*: F_ϕ of A_u symmetry; *gauche*: F_ϕ of A symmetry). This procedure made it possible to obtain reasonable values for the frame amplitudes and perpendicular corrections used in the GED refinements. The symmetrized SQM force fields obtained for the *anti* and *gauche* forms were used in the calculation of similar frame values for all pseudo-conformers which are comprised by the dynamic model.

3.4. The molecular parameters

The geometry of each of the conformers can be described by a set of independent parameters, which were then fitted to the experimental data. In our refinements these parameters were chosen as: r(Si–Si), r(⟨Si–Cl⟩), (average value), r(Si–H), $\angle$(SiSiH), $\angle$(⟨SiSiCl⟩) (average value), P(ClSiCl) (projection angle; the angle between the two Si–Cl bonds projected on a plane perpendicular to the Si–Si bond), the torsional angle parameters ϕ(HSiSiH)$_{anti}$ and ϕ(HSiSiH)$_{gauche}$, along with the two potential constants V_1 and V_3. Ab initio constraints were incorporated as described earlier. The r(Si–H) parameter value could not be refined and was held a constant in the least squares refinements, and the r_α value used was calculated from the assumed r_e ab initio value (MP2) by using the anharmonicity constant $a_3 = 2.0$ Å^{-1} in the usual formula $r_\alpha = r_e + 3a_3l^2/2$. The r_g value is then $r_g = r_e + 3a_3l^2/2 + K$, where K is the perpendicular amplitude correction.

Table 2
Interatomic distances and vibrational amplitudes for the *gauche* conformer of 1,1,2,2-tetrachlorodisilane[a] as obtained from GED/ab initio refinements

| | GED | | | | Ab initio values | |
	r_α	r_g	l_{calc}	l_{exp}	MP2[b] distances	MP4[c] distances
$r(Si–Si)$	2.307(8)	2.310	0.056	0.085(7)	2.337	2.339
$r(Si–Cl_{3,8})$	2.027(2)	2.036	0.048	0.057(3)[d]	2.047	2.051
$r(Si–Cl_{4,7})$	2.034(2)	2.043	0.048	0.057(3)[d]	2.053	2.056
$r(Si–H)$	[1.497]	[1.511]	0.075		1.480	1.469
$r(H_2…Cl_3)$	2.875(9)	2.887	0.112		2.877	2.875
$r(H_6…Cl_7)$	2.899(9)	2.913	0.112		2.880	2.876
$r(H_2…Cl_4)$	2.899(9)	2.913	0.112		2.880	2.876
$r(H_6…Cl_8)$	2.875(9)	2.887	0.112		2.877	2.875
$r(Cl_3…Cl_4)$	3.321(7)	3.329	0.097	0.097(6)[e]	3.368	3.372
$r(Cl_7…Cl_8)$	3.321(7)	3.329	0.097	0.097(6)[e]	3.368	3.372
$r(Si_1…Cl_7)$	3.513(8)	3.518	0.127	0.140(8)[f]	3.559	3.565
$r(Si_5…Cl_4)$	3.513(8)	3.518	0.127	0.140(8)[f]	3.559	3.565
$r(Si_5…H_2)$	3.176(7)	3.182	0.134		3.209	3.207
$r(Si_1…H_6)$	3.176(7)	3.182	0.134		3.209	3.207
$r(Si_5…Cl_3)$	3.553(8)	3.560	0.121	0.134(8)[f]	3.579	3.575
$r(Si_1…Cl_8)$	3.553(8)	3.560	0.121	0.134(8)[f]	3.579	3.575
$r(H…H)$	3.676(8)	3.681	0.208		3.777	3.753
$r(H_6…Cl_4)$	3.887(8)	3.892	0.232		3.876	3.915
$r(H_2…Cl_7)$	3.887(8)	3.892	0.232		3.876	3.915
$r(H_2…Cl_8)$	4.844(7)	4.850	0.125		4.864	4.857
$r(H_6…Cl_3)$	4.844(7)	4.850	0.125		4.864	4.857
$r(Cl_3…Cl_7)$	4.101(19)	4.108	0.220		4.236	4.187
$r(Cl_4…Cl_8)$	4.101(19)	4.108	0.220		4.236	4.187
$r(Cl_3…Cl_8)$	4.149(28)	4.159	0.232		4.074	4.097
$r(Cl_4…Cl_7)$	5.256(11)	5.259	0.108	0.116(18)	5.313	5.328

[a] Distances (r_α, r_g) and amplitudes (l_{ij}) are in ångstrom (Å). Parenthesized values are 2σ, where σ includes estimates of uncertainty in voltage/nozzle heights and of correlation in the experimental data. "Quality of fit" factor for the final refinement was $R = 0.1147$.

[b] MP2/6-31G(d) values.

[c] MP4(SDQ)/6-31++G(d,p) values.

[d] These amplitudes were refined as groups.

[e] These amplitudes were refined as groups.

[f] These amplitudes were refined as groups.

The vibrational properties of the molecule were specified by 28 amplitude parameters for each pseudo-conformer, corresponding to the number of interatomic distances in the molecule, making a total of 364 weighted distances included in the dynamic theoretical model. Many, but not all, of the amplitudes could successfully be refined. Some of the amplitudes were refined together as groups. The amplitudes which could not be refined were kept constant at the values calculated from the SQM force fields utilized in the NCA.

In the final refinement, four geometrical parameters, five amplitude parameters and the potential

constant V_3 were refined simultaneously. The results of this refinement are given in Table 1, where the corresponding geometrical values from the MP2/6-31G(d) ab initio calculations are also given. The interatomic distances, along with refined and calculated vibrational amplitudes (from the SQM force fields) and the MP2- and the MP4-optimized distances are given in Table 2. The correlation matrix for the refined parameters is given in Table 3. In Table 4 are shown the experimentally obtained energy values from the two-term potential function together with the corresponding results from the HF/6-31G(d) calculations. Other calculated values for the confor-

Table 3
Correlation matrix (× 100) for the refined parameters of 1,1,2,2-tetrachlorodisilane

Parameter	σ_{LS}[a]	r_1	r_2	$\angle_3$	$\angle_4$	V_3	l_1	l_2	l_3	l_4	l_5
Si–Si	0.3	100									
Si–Cl	0.03	19	100								
SiSiCl	14	−58	−19	100							
P(ClSiCl)	25	−44	−21	88	100						
V_3	19	23	−12	8	−8	100					
l(Si–Si)	0.2	−19	−35	10	10	−5	100				
l(Si–Cl)	0.05	25	20	−8	−8	9	−46	100			
l(Cl·Cl)	0.2	7	2	−12	−3	9	−16	27	100		
l(Si…Cl)	0.2	2	4	5	21	6	−12	21	66	100	
l(Cl…Cl)$_{anti}$	0.6	7	−2	2	−3	35	−5	8	7	5	100

[a] Standard deviations (× 100) from least-squares refinement. Distances (*r*) and amplitudes (*l*) are in ångstroms; angles (∠) are in degrees.

mational energy differences are also assembled in Table 4. In Table 5, the results for TCDS are compared with the previous GED results for 1,2-diiododisilane and 1,1,2,2-tetraiododisilane [5], 1,1,2,2-tetrabromodisilane [4], disilane [2], hexafluorodisilane [8,9], hexachlorodisilane [3] and 1,2-dichlorotetramethyldisilane [14].

The theoretical intensity curve for the final model is shown in Fig. 2 together with average experimental and difference curves. The corresponding RD curves along with the difference curve are shown in Fig. 3 and the theoretical RD-curves calculated for 100% of each conformer, and the final refined mixture are shown in Fig. 4. Fig. 5 shows the energy values obtained from the dynamic GED model and the HF/6-31G(d) calculations listed in Table 4, plotted as functions of the torsional angle ϕ(HSiSiH) for easy comparison.

4. Discussion

Inclusion of a V_6 constant in the potential function, $V(\phi)$, with a large negative value seemed to improve the fit between the experimental and theoretical radial distribution curves slightly. However, the torsional potential curve resulting from inclusion of this V_6 term was deemed quite unreasonable based on both the potential energy barrier values as well as the general shape of the curve. Refinements on a V_4 potential constant gave values which were insignificantly different from zero. The V_4 and V_6 potential constants were therefore not included in the final refinement,

making the pseudo-conformational distribution dependent on the V_1 and V_3 potential constants only. Our two term cosine potential function for the torsion about the Si–Si bond has a minimum at $\phi = 60°$. This is lower than most of the ab initio results, but quite close to the molecular mechanics value. For ϕ(HSiSiH)$_G$ we found the following values from the different levels of ab initio theory employed: ϕ_G(HF/6-31G(d)) = 66.6°; ϕ_G(MP2/6-31G(d)) = 66.2°; ϕ_G(HF/SBK-ECP) = 69.5° [18]; and ϕ_G(MP4(SDQ-fc)/6-31 + + G(d,p)) = 63.2°. The MM calculated value for this parameter was 59° [17].

Table 2 shows a fairly close agreement in most of the interatomic distances between the experimental GED values and both the MP2- and MP4-optimized distance values, but the Si–Si and the Si–Cl bonds are both calculated longer than the experimental values. The valence angles agree fairly well with the calculated ab initio results. A constant difference value of 0.8° between the *anti* and *gauche* conformers was introduced into the projection angle[P(ClSiCl)], and the projection angle itself was refined to allow better adjustment of the conformational differences in the valence angles compared to the ones obtained theoretically.

The experimentally determined potential constant $V_3 = 1.5 \pm 0.5$ kcal mol^{-1} was obtained from the dynamic model. The V_1 term was not refinable at any reliable level, so it was decided to use the energy information from the FT-Raman spectroscopic work [18] in a direct manner, as this V_1 term solely determines the conformer energy difference. Therefore, the IR/Raman energy difference value of − 0.45 ±

Table 4
Relative energies (kcal mol^{-1}) for 1,1,2,2-tetrachlorodisilane as obtained from various theoretical and experimental methods

$\Delta E(\phi)$ ϕ(HSiSiH)	HF/6-31G(d)[a]	HF/SBK-ECP[a]	MP2/6-31G(d)	MP4(SDQ)/6-31 + + G(d,p)	Molecular mechanics	Exp. GED[b]	Exp. Raman
0	2.42				2.2	1.35	
30	1.49					0.64	
60 (*gauche*)	0.51	0.50	0.27	0.35	0	0	0
90	0.82					0.90	
120	1.22				2.5	1.80	
150	0.50					1.16	
180 (*anti*)	0	0	0	0	0.7	0.45	0.45(17)
Ref.	This work	[18]	This work	This work	[17]	This work	[18]

^{a} These ab initio energy values are not corrected with the ZPE difference. The ZPE-corrected *gauche* values would be about 0.56 kcal mol^{-1}, by applying the MP2-calculated ZPE difference value (0.0532 kcal mol^{-1} in favor of *anti*).

^{b} Energy values as calculated by using the obtained potential constants, V_1 and V_3, in the two-term potential function described in the text.

Table 5
Comparison of results from GED investigations of eight closely related disilanes[a] (X = H, F, Cl, Br, I)

Parameter Bond type	IH$_2$Si–SiH$_2$I r_g	I$_2$HSi–SiHI$_2$ r_g	Br$_2$HSi–SiHBr$_2$ r_g	Cl$_2$HSi–SiHCl$_2$[b] r_g	H$_3$Si–SiH$_3$ r_g	F$_3$Si–SiF$_3$ r_α(0)	Cl$_3$Si–SiCl$_3$ r_a	ClMe$_2$Si–SiMe$_2$Cl r_a
r(Si–Si)	2.380(34)	2.389(37)	2.350(19)	2.310(8)	2.331(3)	2.317(6)	2.324(30)	2.338(13)
r(Si–X)	2.429(13)	2.440(9)	2.206(5)	2.039(2)	–	1.564(2)	2.009(4)	2.077(2)
r(Si–H)	1.510(25)	1.50^c	1.490^c	1.511^c	1.492(3)	–	–	–
∠SiSiX	107.5(12)	107.2(10)	107.1(12)	108.9(4)	–	109.2(6)	109.7(6)	107.7(6)
∠XSiX	–	111.4(6)	110.1(16)	109.7(3)	108.6(4)	108.6(3)	–	–
∠SiSiH	111.9(157)	111.9^c	108.6^c	111.5^c	110.3(4)	–	–	–
∠XSiH	107.9(170)	109.6(8)	–	108.9(5)	–	–	–	–
r(X...X)$_{anti}$	5.97	5.97	5.54	5.26	–	–	–	5.36
r(X...X)$_{gauche}$	4.41	4.45	4.19	4.11	–	–	–	4.33
ϕ(anti)^d	180	180	180	180	–	–	–	180
ϕ(gauche)^d	58(31)	61(27)	60^e	60^c	–	–	–	76.5(25)
$\alpha \times 100$ (gauche)^f	76(16)	60(29)	50(20)	80	–	–	–	83(11)
Ref.:	[5]	[5]	[4]	This work	[2]	[8,9]	[3]	[14]

^{a} Distances are in ångstroms (Å), angles (∠α) in degrees.

^{b} *Gauche* values.

^{c} Assumed value.

^{d} Torsion angles. For *anti* a C$_{2h}$ symmetry was used (torsional angles of exactly 180°).

^{e} Studied by using a dynamic model.

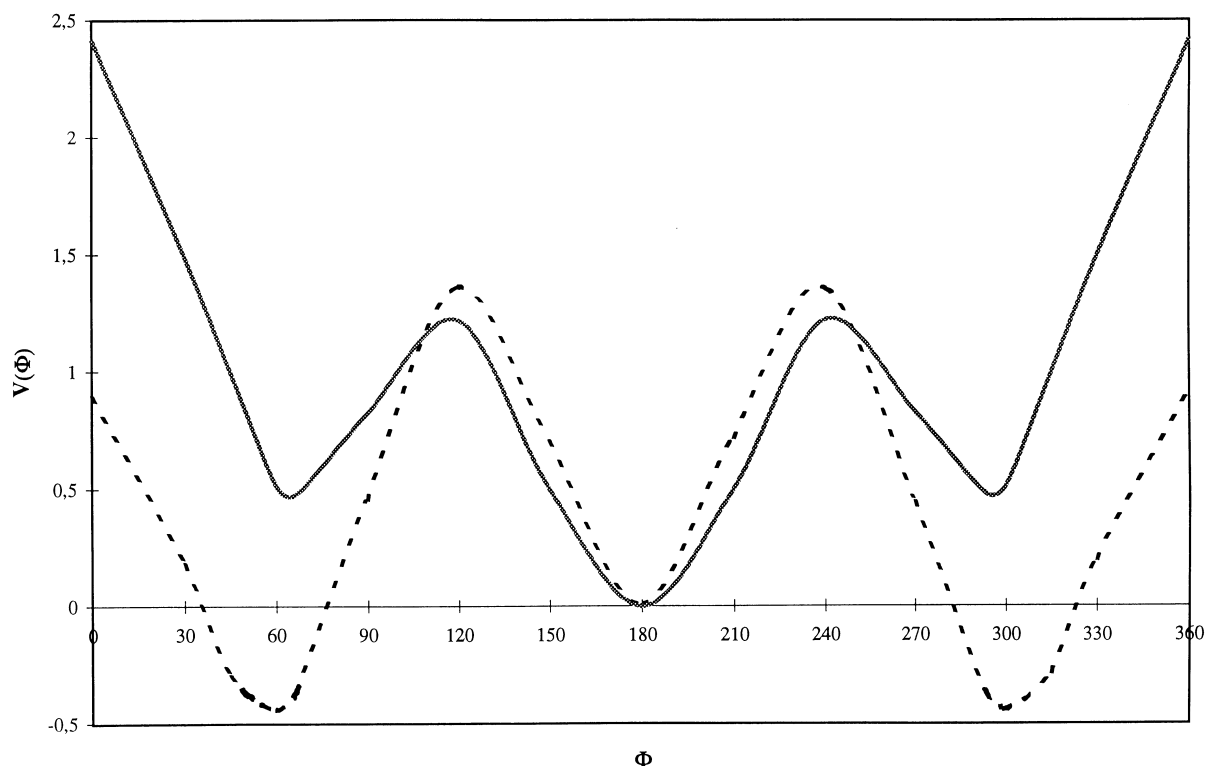^{f} Estimated percentage of the *gauche* conformer observed in the gas phase.

Fig. 5. Torsional potential curves for 1,1,2,2-tetrachlorodisilane, as obtained from ab initio MO HF/6-31G(d) energy values and as obtained from the GED data using a dynamic model, showing the potential energy $V(\phi)$ (kcal mol^{-1}) as a function of the torsional angle ϕ(HSiSiH) (cf. Table 4). The solid line shows the ab initio potential, while the broken line shows the curve resulting from the two-term potential function described in the text.

0.17 kcal mol^{-1} indicated that $V_1 = -0.6$ kcal mol^{-1} which was utilized in the final refinement. A reasonable error estimate for V_1 would then be ± 0.2 kcal mol^{-1}, based on the reported error in the Raman energy value. The experimental results for the conformer energy difference are not supported by any of the ab initio calculations. As shown in Table 4, only the empirically based MM-calculations [17] predicted the *gauche* conformer to be the more stable (by about 0.7 kcal mol^{-1}). As the MM-calculations were based on previously observed gas-phase data for the haloalkanes, this was not surprising, because only H…Cl, Cl…Cl and H…H interactions contribute to the non-bonded potentials important for conformational stability. The silicon atoms only contribute to the bonded stretch and bend through reference values for the bonded distances, angles and the valence force constants [17].

The four different levels of ab initio calculations shown in Table 4 predicted *anti* as the more stable form, including the high-level MP4(SDQ-fc) calculations. The ab initio values were found in the range 0.27–0.56 kcal mol^{-1}, when the MP2 ZPE correction was applied. They are not in agreement with the FT-Raman value. It should be noted that for the alkane analog, 1,1,2,2-tetrachloroethane, ab initio calculations at the HF/6-31G(d) level gave the *anti* conformer lower energy by 0.32 kcal mol^{-1} [38], which is in fairly good agreement with the experimental value obtained from the GED data analysis (0.1 ± 0.1 kcal mol^{-1}) [38]. Thus, ab initio calculations seem to be able to reproduce the conformer energy difference for the alkane better than for the corresponding disilane.

The HF/6-31G(d) calculations gave a torsional potential curve for the rotation about the Si–Si bond in TCDS (Fig. 5). The ab initio potential energy barriers may be compared with the values obtained

from MM [17] and the potential barriers obtained from the present GED analysis. The HF/MM/GED values are (kcal mol^{-1}): *Gauche → Gauche*: 1.9/2.2/ 1.4; *Gauche → Anti*: 0.7/2.5/1.8, and *Anti → Gauche*: 1.2/1.8/1.4. The large difference in the *Gauche → Anti* barrier between the ab initio result and the other two estimates arises from the disagreement in conformer stability as obtained by the methods, cf. Table 4. Also, it should be emphasised that the GED values are strongly influenced by the Raman study [18] through the V_1 potential constant, as discussed before.

In Table 5 results obtained from investigations of several related halogenated disilanes, including TCDS, were compared [2–5,8,9,14]. Two of the molecules were found to prefer the *anti* conformation (1,1,2,2-tetraiodo- and tetrabromodisilane), while in 1,2-diiododisilane and TCDS the *gauche* conformation was found lower in energy, though the observations were quite uncertain. For $Cl_2MeSi–SiMeCl_2$, the *anti* conformer was found to be more stable [16] by Raman spectroscopy in the liquid phase, by 0.25 ± 0.05 kcal mol^{-1}, while in $ClMe_2Si–SiMe_2Cl$ the *gauche* form was found more stable by 0.6 ± 0.5 kcal mol^{-1} [14], by the use of GED. Thus, discussing these six molecules only, all tetrahalogenated disilanes except for TCDS show *anti* preference, while the disubstituted ones and TCDS show *gauche* preference.

The pattern which may be drawn from these experimental data is that the disilanes seem to prefer conformations in which not more than two X…X *gauche* interactions occur at one time (X = halogen), where the halogen atoms are larger than or equal to chlorine. The experimental GED data suggested that both the tetrabromo- [4] and the tetraiododisilane [5] had the *anti* form as the lower-energy conformer. These two molecules have two interactions of each type in the *anti* form. A similar behavior was found in $Cl_2MeSi–SiMeCl_2$ [16], which also had *anti* as the lower-energy conformer. The dihalogenated disilanes 1,2-diiododisilane [5] and $ClMe_2Si–SiMe_2Cl$ [14] can have only one X…X *gauche* interaction, and by definition only when in the *gauche* conformation, and for these molecules *gauche* was found to be lower in energy. These experimental data seem to support the validity of the ''*gauche* effect'' [19].

The only molecule with preference for three X…X

gauche interactions was the TCDS molecule, for which the *gauche* conformer was found to be more abundant in the gas phase (summed contribution from the pseudo-conformers 0–105° amounts to 80%). Here, the three X…X *gauche* interactions seem to stabilize the *gauche* over the *anti* form, this may be observed from the RD-curves (Fig. 4). The obtained $(Cl…Cl)_{gauche}$ distance range (3.9–4.3 Å) are quite close to the minimum in the Morse potential, which is typically about 3.8 Å for this interaction, as used in the MM-calculations [17,39], and also as pointed out by Kveseth [14]. Substituting the small H-atoms with methyl groups, as in $Cl_2MeSi–SiMeCl_2$ [16], seems to make the *gauche* form more energetically unfavorable, probably because of the increased steric strain caused by the two methyl-groups in this molecule.

The Si–Si bond length in the disilanes shown in Table 5 seems to be determined both by the size and the electronegativity of the substituents. The longest Si–Si bonds are found in molecules with large substituents (and lower electronegativity), such as I or Br, the shortest bonds are found in molecules with small substituents, such as H, or substituents with high electronegativity, such as Cl or F. In the three chlorine-substituted molecules, the length of the Si–Cl bond, as expected, decreases with increasing number of chlorine atoms from 2.077(5) Å in 1,2-dichlorotetramethyldisilane [14] to 2.009(4) Å in hexachlorodisilane [3].

However, safe conclusions about geometrical trends or conformer stabilities for the disilanes discussed are not easily drawn as the collection of reliable experimental data is quite limited, and additional halogenated disilanes should be investigated in future work.

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