The Molecular Structure of (Dichloromethyl)-trichlorosilane

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The molecular structure of (dichloromethyl)-trichlorosilane has been determined by gas phase electron diffraction. It has been found that the effective structure of the molecule has C_1-symmetry with an angle of rotation τ and a tilt angle ψ of the $SiCl_3$-group. Several vibrational amplitudes were fixed at values calculated from transferred Urey-Bradly force constants.

Systematic errors resulting from the uncertainties of the fixed parameters have been calculated applying the rules of error propagation. The most important structural parameters (r_g in Å, angles in degrees) are: r(Si-C) = 1.905(10), r(Si-Cl) = 2.019(1), r(C-Cl) = 1.774(4), r(C-H) = 1.16(4), $\sphericalangle$(C-Si-Cl) = 109.8(3), $\sphericalangle$(Si-C-Cl) = 111.4(8), ψ = 4.1(1.0), τ = 6.7(1.4) (the errors in parenthesis include the systematic contributions).

Comparison is made with structural data of other representatives of the series $CH_{3-m}Cl_mSiCl_3$ (m = 0, 1, 2, 3).

Introduction

In many investigations (see [1] and references cited therein) on silicon containing compounds irregularities in the behaviour of molecular properties were discussed in terms of the $(p\text{–}d)_\pi$ back bonding hypothesis. However, Oberhammer and Dakkouri [2] presented evidence that the $(p\text{–}d)_\pi$ bond hypothesis is just a comprehensive description for various contributions of similar order. These contributions are electronic interaction, steric interaction, and the order of hybridization. Depending on the kind of the substituent these contributions are additive or compensate each other partly or totally. The consequence of additive contributions would be a strengthening of the Si-X bond (X is mainly a substituent with high electron density): This is normally called a $(p\text{–}d)_\pi$ bond. With compensating contributions, however, no $(p\text{–}d)_\pi$ bond is to be expected. We cannot expect that from one member of chlorosubstituted methyl silanes the various contributions to observed bond lengths and bond angles can be derived separately. Therefore we have started to collect data on the molecular structures in the series $CH_{3-m}Cl_mSiH_{3-n}Cl_n$ ($m, n = 0, 1, 2, 3$) in order to contribute to the understanding of the character of the Si-C and Si-Cl bond. As a first contribution we report in this work the molecular structure of dichloromethyltrichlorosilane ($CHCl_2SiCl_3$, DCMTS) as obtained by gas phase electron diffraction.

Experimental

The sample of DCMTS has been purchased from PCR Inc., Gainesville, Florida. The purity was checked on the IR spectrum before and after the diffraction experiment. No detectable impurity was found.

Diffraction intensities were recorded with the Balzers Diffractograph KD-G2 [3] in Tübingen at two camera distances. An accelerating voltage of $\simeq$60 KV was used. For all recordings the nozzle temperature was kept at 40 °C and the sample temperature at 20 °C. Four plates per camera distance were selected for the structure determination. Table 1 summarizes the experimental conditions.

Reduction of Data

The transmission values of the photographic plates were recorded with the microdensitometer ELSCAN E-2500 [4] using a step width of Δr = 0.1 mm. These values were reduced to the modified molecular intensity $s \cdot M(s)$ (interpolated with a step width of $\Delta s = 0.2$ Å^{-1}) in the usual way [5] for each photographic plate separately. The program DENSITY by Roszondai et al. [6] proved helpful in fixing the centers of the photographic plates, and thereby the s-scale.

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Distance (mm)	P camera (Torr)	Exposure times (s)	Wavelength λ(Å)	s-range used (Å^{-1})	Range of unit weights (Å^{-1})
250	$\simeq 1 \cdot 10^{-6}$	40—120	0.048868(40)	7.2—34.2	10.0—28.0
500	$\simeq 5 \cdot 10^{-6}$	15— 30	0.048679(42)	1.8—17.6	5.0—14.0

Table 1. Experimental conditions for the diffraction experiments.

For the structure calculations the molecular intensities were entered as averages of the $s \cdot M(s)$-functions from different plates for the respective camera distances. The procedure described in [7] was followed. Diagonal weights were employed in the fitting procedure as described in Ref. [7]; the range of unit weights has been included in Table 1.

During the fitting procedure several vibrational amplitudes had to be fixed. The values adopted were calculated from a model UBFF with force constants transferred from $CH_2ClSiCl_3$ [8], $C_2H_5CCl_2CH_3$ [9], and $(CH_3)_2CHSiCl_3$ [10]. For the structure calculations it was found very useful to employ Marquardt's nonlinear variant [11] of the usual fitting procedure by weighted least squares. Also with molecules as small as $CHCl_2SiCl_3$ it is found rather frequently that the sum of weighted squared residuals is increased in successive iteration steps of uncontrolled least squares fitting. Difficulties of this kind are eliminated by Marquardt's procedure.

Structure Calculations

For the structure calculations DCMTS was assumed to have an equilibrium configuration of C_s-symmetry. Unfortunately the r_a-structure observed in the diffraction experiment is affected by shrinkage effects and does not necessarily show the symmetry of the equilibrium configuration. In particular this implies that nonbonded distances may differ significantly from distances calculated on the basis of a consistent geometry and these should be treated as independent variables. Actually the attempts for the calculation of a r_a-structure of DCMTS on the basis of a consistent geometry of C_s-symmetry resulted in values for the nonbonded anti-Cl...Cl distances which were too large by $\simeq 0.04$ Å. This indicates that shrinkage effects are not negligible.

In this situation the best way would be to calculate all shrinkages and to obtain the r_α-structure. However a closer examination shows that a much simpler approach can be followed. The shrinkage of the non-bonded anti-Cl...Cl distance is essentially due to the torsional motion about the Si-C bond. As shown by Vilkov et al. [12] in cases of high or intermediate barrier height an effective structure can be obtained by giving up the symmetry of the equilibrium configuration and allowing for an effective torsional angle τ of the top group. The "experimental" torsional angle is then a measure for the barrier height. Thus our calculations are based on the following model: (cf. Figure 1):

1) The $SiCl_3$-group is assumed to have local C_{3v}-symmetry.
2) The $CHCl_2$-group has local C_s-symmetry.
3) The molecular C_s-symmetry of the equilibrium configuration is distorted to C_1-symmetry by a rotation of the $SiCl_3$-group about its symmetry axis by a torsional angle τ.
4) All calculations were repeated with additional allowance for a tilt ψ of the C_3-axis of the $SiCl_3$-group off the Si-C bond.

In the course of the calculations a number of parameters had to be fixed to reasonable values due to excessive correlations. Unfortunately this is particularly true for the vibrational amplitude l(Si-C): on the basis of a consistent model at best 5 parameters can be derived from the peak at 2 Å. We decided to fix l(Si-C) to the value calculated from the model force field: this choice has the least influence on the results for the remaining parameters.

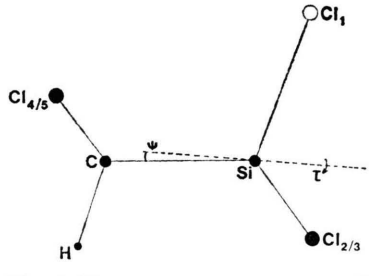

Fig. 1. Projection of the atoms in DCMTS into the symmetry plane with numbering of the atoms and definition of tilt ψ and torsion τ.

However the systematic errors of a number of parameters is largely increased by keeping this parameter constant (see below).

The final results are summarized in Table 2 for $\psi \equiv 0$. The results including ψ as adjustable parameter are summarized in Table 3. Figure 2 shows the experimental and best fit theoretical reduced molecular intensities. The corresponding radial distribution functions are shown in Figure 3.

In Tables 2 and 3 three different errors are given: ε_1 is the single standard error of the fit, ε_2 is due to the error propagation (see appendix) from the estimated uncertainties of the fixed parameters, and the total error $\sigma = \sqrt{6\varepsilon_1^2 + 3\varepsilon_2^2}$ is near to three times the standard error of the fit. For the calculation of ε_2 we assumed that the uncertainty of the angle $\sphericalangle$(Si-C-H) is 5° while the uncertainties of the fixed vibrational amplitudes were assumed to be 10% of the calculated value. Note that the error ε_2 is of the same order as ε_1. The calculation of ε_2 showed clearly that the largest contribution comes from the fixed vibrational amplitude l(Si-C). In order to investigate this point further we have recalculated all parameters with l(Si-C) fixed at different values ranging from 0.054 Å to 0.074 Å. We observe a slight decrease of the sum of weighted

Table 2. Geometrical parameters and vibrational amplitudes of DCMTS without tilt ψ. $\sum$ is the sum of weighted squared residuals, R the index of resolution [7]. a) The angle $\sphericalangle$(Cl-C-H) has been calculated by means of the redundancy condition. For errors see text.

	r_a	ε_1	ε_2	σ
r(Si-Cl)	2.0170	0.0004	0.0002	0.0010
r(Si-C)	1.8881	0.0040	0.0010	0.0099
r(C-Cl)	1.7682	0.0014	0.0008	0.0038
r(C-H)	1.1768	0.0168	0.0038	0.0416
$\sphericalangle$(C-Si-Cl)	109.58	0.09	0.09	0.28
$\sphericalangle$(Si-C-Cl)	112.30	0.28	0.27	0.84
$\sphericalangle$(Si-C-H)	109.47	fix	—	—
$\sphericalangle$(Cl-C-Cl)	109.17	0.29	0.07	0.72
$\sphericalangle$(Cl-C-H)	106.64	a)	—	—
torsion τ	6.10	0.64	0.22	1.61
l(Si-Cl)	0.0507	0.0004	0.0004	0.0013
l(Si-C)	0.0537	fix	—	—
l(Si ... Cl)	0.0871	0.0038	0.0018	0.0099
l(Si ... H)	0.1171	fix	—	—
l(C-Cl)	0.0676	0.0019	0.0012	0.0051
l(C-H)	0.0789	fix	—	—
l(C ... Cl)	0.0983	fix	—	—
l($Cl_{1/2}$ ... $Cl_{2/3}$)	0.0968	0.0017	0.0009	0.0044
l(Cl_4 ... Cl_5)	0.0951	0.0069	0.0043	0.0186
l(Cl_1 ... $Cl_{4/5}$)	0.2991	0.0157	0.0074	0.0404
l($Cl_{2/3}$ ... $Cl_{4/5}$)	0.1195	0.0112	0.0056	0.0290
l(Cl ... Cl)$_{anti}$	0.1088	0.0020	0.0004	0.0050
l($Cl_{4/5}$ ... H)	0.1055	fix	—	—
l(Cl_1 ... H)	0.1197	fix	—	—
l($Cl_{2/3}$ ... H)	0.1870	fix	—	—
$\sum$	$3.27 \cdot 10^{-2}$			
R_{500}	4.33			
R_{250}	7.53			

Table 3. Geometrical parameters and vibrational amplitudes of DCMTS with inclusion of tilt ψ (cf. Table 2).

	r_a	ε_1	ε_2	σ
r(Si-Cl)	2.0178	0.0003	0.0002	0.0009
r(Si-C)	1.9036	0.0038	0.0011	0.0096
r(C-Cl)	1.7717	0.0012	0.0010	0.0034
r(C-H)	1.1643	0.0139	0.0086	0.0372
$\sphericalangle$(C-Si-Cl)	109.84	0.10	0.04	0.26
$\sphericalangle$(Si-C-Cl)	111.40	0.25	0.28	0.78
$\sphericalangle$(Si-C-H)	109.47	fix	—	—
$\sphericalangle$(Cl-C-Cl)	109.25	0.30	0.06	0.74
$\sphericalangle$(Cl-C-H)	107.59	a)	—	
torsion τ	6.76	0.58	0.07	1.42
tilt ψ	4.11	0.42	0.15	1.05
l(Si-Cl)	0.0517	0.0004	0.0005	0.0014
l(Si-C)	0.0537	fix	—	—
l(Si ... Cl)	0.0904	0.0025	0.0063	0.0125
l(Si ... H)	0.1171	fix	—	
l(C-Cl)	0.0633	0.0015	0.0019	0.0048
l(C-H)	0.0789	fix	—	
l(C ... Cl)	0.0983	fix	—	
l($Cl_{1/2}$ ... $Cl_{2/3}$)	0.0954	0.0014	0.0022	0.0052
l(Cl_4 ... Cl_5)	0.0810	0.0035	0.0077	0.0158
l(Cl_1 ... $Cl_{4/5}$)	0.2859	0.0125	0.0123	0.0372
l($Cl_{2/3}$ ... $Cl_{4/5}$)	0.1092	0.0083	0.0031	0.0211
l($Cl_{3/2}$ ... $Cl_{4/5}$)	0.1075	0.0017	0.0005	0.0042
l($Cl_{4/5}$ ... H)	0.1055	fix	—	—
l(Cl_1 ... H)	0.1197	fix	—	—
l($Cl_{2/3}$ ... H)	0.1870	fix	—	—
$\sum$	$2.30 \cdot 10^{-2}$			
R_{500}	3.38			
R_{250}	6.61			

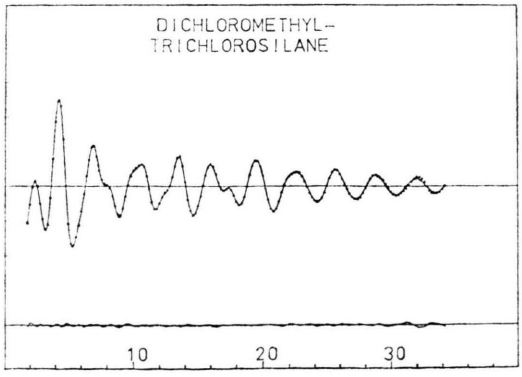

Fig. 2. Experimental and best fit theoretical molecular intensity $s \cdot M(s)$ of DCMTS.

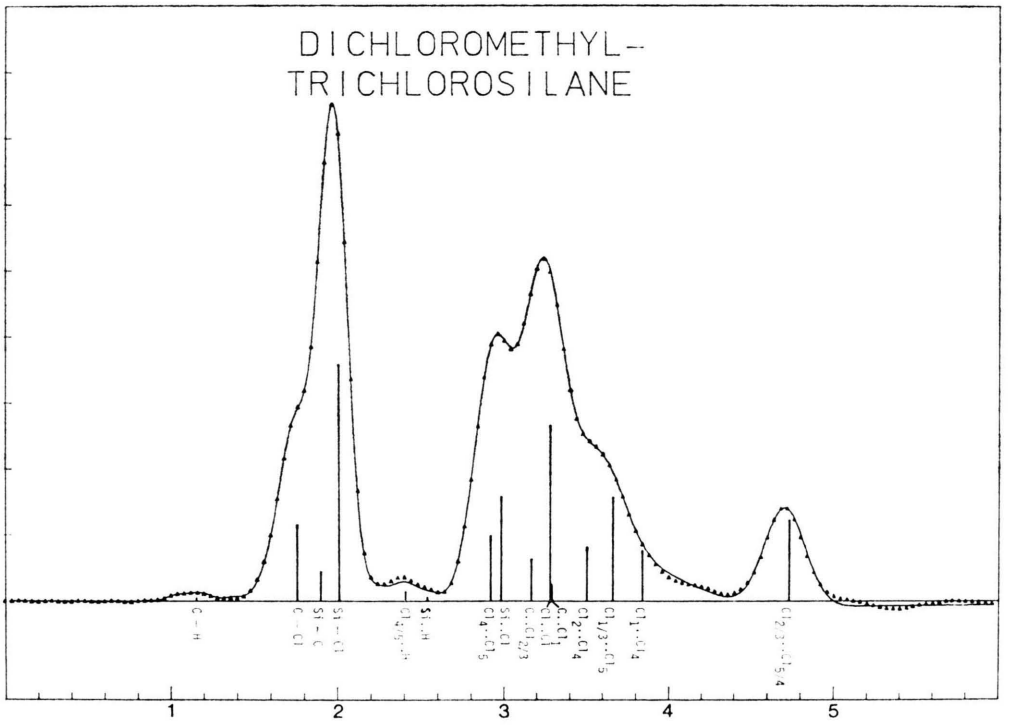

Fig. 3. Experimental and best fit theoretical radial distribution function $f(r)$ of DCMTS.

squared residuals $\sum$ with increasing l(Si-C) and an approximately linear variation of the fitted parameters. However in all cases the changes of the parameters were less than the total error given in Table 3.

Discussion

Comparing Table 2 and Table 3 we find that the introduction of the tilt ψ of the perchloro silyl group has a considerable effect on the resulting bond lengths, bond angles and vibrational amplitudes. In particular the shift of 0.014 Å in the Si-C distance seems significant. Taking into account the reduction in the sum of weighted squared residuals $\sum$ by a factor 1.4 the tilt appears to be an important parameter. The value $\psi = 4.1°$ is of reasonable size and the direction corresponds to that which is to be expected from a consideration of steric hindrance and electrostatic repulsion. We therefore prefer the results of Table 3.

In Table 4 we give a comparison of some bond lengths and bond angles in the series $CH_{3-m}Cl_mSiCl_3$ ($m = 0, 1, 2, 3$) and in Fig. 4 we show the dependence of the Si-C distance on the number of chlorine atoms in the methyl group. Obviously the observed distances are consistent with the assumption that

Table 4. Comparison of various bond lengths and bond angles in $CH_{3-m}Cl_mSiCl_3$ compounds.

Molecule	C-Si	C-Cl	Si-Cl	C-Si-Cl	Si-C-Cl	Ref.
CH_3SiCl_3	1.876	—	2.021	109.5	—	[13], r_0
	1.848	—	2.026	110.3	—	[14], r_s
$CH_2ClSiCl_3$	1.851 (10)	1.794	2.028	109.95	111.7	[15], r_g
$CHCl_2SiCl_3$	1.905 (10)	1.774	2.019	109.8[a]	111.4	this work, r_g
CCl_3SiCl_3	1.932	1.771	2.018	108.6	109.1	[16], r_g

[a] Due to the presence of the tilt ψ and the torsion τ only an average angle $\sphericalangle$C-Si-Cl can be given.

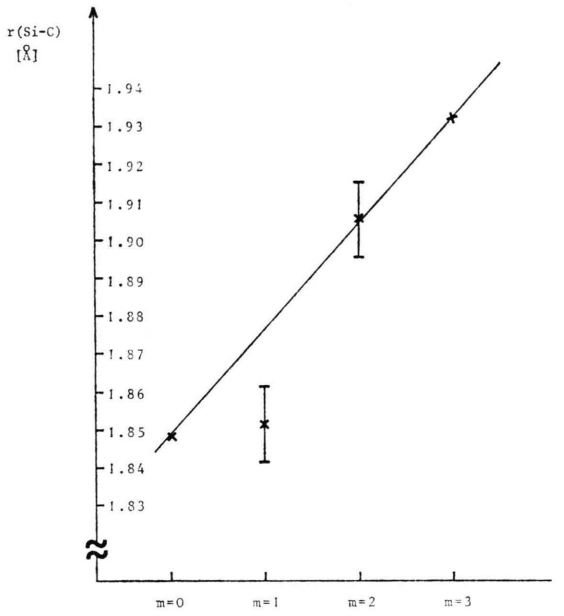

Fig. 4. Dependence of the Si-C bond distance on the number of chlorine atoms in $CH_{3-m}Cl_mSiCl_3$.

the Si-C bond distance increases linearly with the number of the chlorine atoms in the methyl group. The only exception is found with the Si-C distance in $CH_2ClSiCl_3$. We should add at this point that in contrast to the value given by Vajda et al. [15] our own investigation [16] on this molecule resulted in a bond length which is larger than that expected from Figure 4. Thus we conclude that the situation in $CH_2ClSiCl_3$ is not yet completely understood.

The "experimental" torsional angle τ allows an estimation of the barrier to internal rotation of the $SiCl_3$ group. Using the formula derived by Vilkov et al. [12] we obtain $V_3 = 6 \pm 3$ kcal/mol. This value is in reasonable agreement with the potential barrier found for CCl_3SiCl_3 [17] and $CH_2ClSiCl_3$ [8, 15].

It is worthwhile to note that the influence of increasing chlorination of the methyl group on the Si-C bond distances is much stronger than the influence of increasing chlorination of the silyl group: in going from methyl silane [18] to methyl trichlorosilane the distance changes by $\delta r = 0.019$ Å. The corresponding variation in going from methyl trichlorosilane to perchloro methyl silane is $\delta r = 0.084$ Å. This difference demonstrates that the bond character in $CH_{3-m}Cl_mSiH_{3-n}Cl_n$ has to be discussed by consideration of the hybridization as well as electrostatic repulsion and inductive contributions.

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Appendix

In many investigations the number of model parameters exceeds the number of parameters which can be deduced from the experimental data. In these cases several deliberately chosen model parameters have to be fixed to reasonable values. However this introduces systematic errors into the fitted parameters due to the uncertainties of the fixed parameters. We assume that this systematic error can be estimated by the rule for error propagation:

$$\sigma^2(P_{\text{fitted},i}) = \sum_{K=1}^{r} \left(\frac{\partial P_{\text{fitted},i}}{\partial P_{\text{fixed},K}} \cdot \sigma(P_{\text{fixed},K}) \right)^2 ,$$

where r is the number of fixed parameters and $\sigma(P_{\text{fixed},K})$ is the estimated uncertainty of the K'th parameter kept fix. We then have to calculate the partial derivatives $\partial P_{\text{fitted},i}/\partial P_{\text{fixed},K}$.

The required partial derivatives are obtained in the following way: Let A be the Jacobian matrix: $A = (\partial O/\partial P)$, with O the experimental observations and P the set of model parameters. Let also G be the weight matrix and b the right hand side of the system of equations of condition

$$A\,P = b\,. \tag{A1}$$

Then the least squares criterion requires that the norm of $G^{1/2} \cdot b$ be a minimum with respect to the parameters P. The solution to this problem is well known:

$$P = (A^{\mathrm{T}} G A)^{-1} A^{\mathrm{T}} G\, b\,. \tag{A2}$$

If we fix some parameters Eq. (A1) can be rearranged by reordering the parameters to give

$$A_1 P_{\text{fitted}} + A_2 P_{\text{fixed}} = b\,. \tag{A3}$$

Now we wish to minimize the norm of

$$G^{1/2}(b - A_2 P_{\text{fixed}})$$

with respect to the set of parameters P_{fitted}. The result is

$$P_{\text{fitted}} = (A_1{}^{\mathrm{T}} G A_1)^{-1} A_1{}^{\mathrm{T}} G (b - A_2 P_{\text{fixed}})\,. \tag{A4}$$

Equation (A4) shows directly the dependance of P_{fitted} on P_{fixed} giving for the partial derivatives

$$\frac{\partial P_{\text{fitted},i}}{\partial P_{\text{fixed},K}} = -[(A_1{}^T G A_1)^{-1} A_1{}^T G A_2]_{i,K}. \qquad \text{(A5)}$$

Thus if we calculate the Jacobian with respect to all model parameters the required derivatives are obtained simply by some matrix manipulations.

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