

Journal of Organometallic Chemistry, 188 (1980) 321–327
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTRON DIFFRACTION AND VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF THE MOLECULAR STRUCTURE OF (CHLOROMETHYL)TRICHLOROSILANE

E. VAJDA, T. SZÉKELY, I. HARGITTAI *,

Hungarian Academy of Sciences, Research Laboratory for Inorganic Chemistry, Budapest (Hungary)

A.K. MALTSEV, E.G. BASKIR, O.M. NEFEDOV,

N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

and J. BRUNVOLL

Department of Physical Chemistry, The University of Trondheim, Trondheim-NTH (Norway)

(Received October 11th, 1979)

Summary

An electron diffraction analysis of the molecular structure of the title compound has been carried out, and related vibrational spectroscopic measurements and calculations have been made. The main bond lengths (r_g) and bond angles (r_α) are as follows: Si—Cl, 202.8(2); Si—C, 185.1(10); C—Cl, 179.4(11); C—H, 111.2(18) pm; Si—C—Cl, 111.7(4); Cl—Si—C, 109.95(21)°. The conformation of the molecule is staggered. The barrier to internal rotation is estimated to be around 10 kJ mol⁻¹.

Introduction

Variations in the molecular geometries of simple derivatives of silane have recently been reviewed [1]. One of the characteristic features of these variations is the sensitivity of the geometry to the changes in the number of the halogen atoms attached to the silicon atom. To extend structural information on this type of compound we have determined the molecular geometry of (chloro-

* Budapest, P.O. Box 117, H-1431.

romethyl)trichlorosilane. An electron diffraction analysis was augmented by vibrational spectroscopic measurements and calculations.

Sample

$\text{CH}_2\text{ClSiCl}_3$ was isolated by fractional distillation from the products of chlorination of CH_3SiCl_3 . The mass spectrum and GLC analysis of the sample showed it to be >99% pure.

Vibrational spectroscopy

The IR spectra of $\text{CH}_2\text{ClSiCl}_3$ were obtained in the gas, liquid and solid (77 K) phases as well as in an Ar-matrix (10 K) with the IKS-24 ("LOMO") and Hitachi-225 grating spectrophotometers. The Raman laser spectra (Spex Ramalog-6 instrument with an argon laser, 514.5 nm) were recorded for the liquid. Most of the frequencies agree with published data [2]; the values listed in Table 1 are from the IR spectrum of solid $\text{CH}_2\text{ClSiCl}_3$ (77 K) and from the Raman spectrum of the liquid. Matrix isolation spectra showed additional isotopic splitting due to chlorine isotopes.

Our vibrational assignments differ from those in the literature [2]. The IR band at 746 cm^{-1} is assigned to the Si-C stretching vibration, because the frequency of the latter in CH_3SiCl_3 (763 cm^{-1} [3]) and in other chloromethylsilanes is generally above 700 cm^{-1} [4]. A new assignment of the 798 cm^{-1} band to the CH_2 rocking mode is consistent with the rather high frequency of this vibration in $\text{CH}_2\text{ClSiH}_3$ (815 cm^{-1} [5]) and in $\text{CH}_2\text{ClSi}(\text{CH}_3)\text{Cl}_2$ (791 cm^{-1} [2]). The assignments (Table 1) are in agreement with normal coordinate calculations performed with a modified Schachtschneider's program [6]. The force constants were taken mainly from CH_3SiCl_3 vibrational analysis [3].

TABLE 1
VIBRATIONAL FREQUENCIES OF $\text{CH}_2\text{ClSiCl}_3$ (cm^{-1})

Infrared (solid, 77K)	Raman (liquid)	Approximate description
2983		CH stretching
2933		CH stretching
1383		CH_2 scissoring
1186		CH_2 wagging
1101		CH_2 twisting
798		CH_2 rocking
746		CSi stretching
684		CCl stretching
604.5		SiCl stretching
590		SiCl stretching
457		SiCl stretching
	284	ClCSi deformation
	221	SiCl_3 rocking
	(220)	SiCl_3 deformation
	172	SiCl_3 deformation
	105	SiCl_3 deformation
	80	SiCl_3 rocking
	67	SiCl_3 torsion

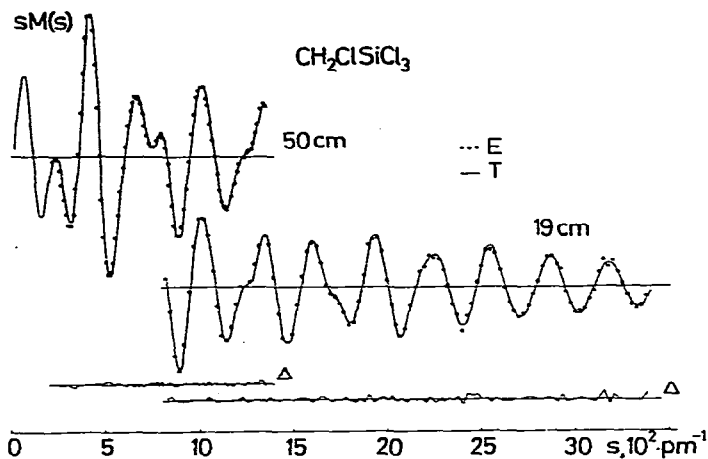


Fig. 1. Experimental (E) and theoretical (T) molecular intensities and the difference curves.

Electron diffraction

The electron diffraction patterns were recorded at a nozzle temperature of about 36°C in the EG-100A unit of the Budapest laboratory [7–9]. For details of data treatment and scattering functions used see ref. 10. The reduced molecular intensities and the radial distributions are shown in Figs. 1 and 2. As the contribution of the anti Cl...Cl distance can be easily assigned from the experimental radial distribution, the molecular conformation is unambiguously determined to be staggered, as illustrated by a Newman projection in Fig. 3.

C_s symmetry was assumed for the molecule as a whole in some of the structure refinements, while in others deviation from this symmetry by rotation

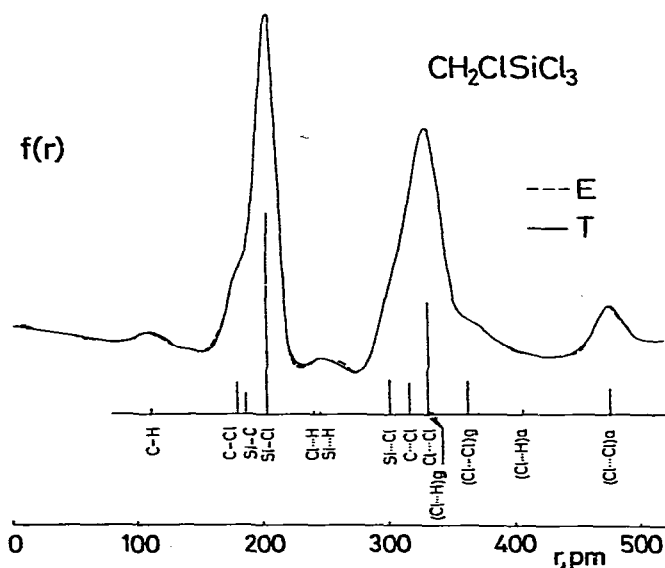


Fig. 2. Experimental (E) and theoretical (T) radial distributions. The individual interatomic distances and their relative weights are indicated by vertical bars.

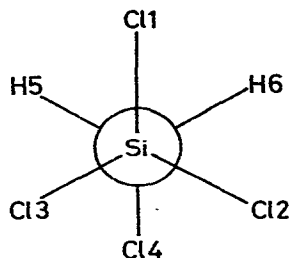


Fig. 3. Newman projection of the molecular model of $\text{CH}_2\text{ClSiCl}_3$ representing view along the Si—C bond and the numbering of atoms.

around the Si—C bond was allowed. The SiCl_3 group was assumed to have C_3 symmetry with the Si—C bond coinciding with the symmetry axis in most cases. The bond angles H—C—Cl and H—C—Si were assumed to be 109.5° .

The structural parameters were refined by the least-squares technique based on the molecular intensities [11]. Both the above mentioned refinement schemes produced good agreement with the experimental data, except that in the case of the C_s symmetry constraint slight discrepancies occurred between the radial distribution and experimental curves in the region of the contributions from the rotation-dependent interactions. Additionally, another scheme was employed in which the rotation-dependent distances were treated as independent parameters.

The results from the three different refinement schemes are listed in Table 2. The standard deviations of the least-squares refinement are also cited. The final results are given in Table 3 in terms of r_g bond lengths and r_α bond angles. The estimated error limits were obtained in the following way:

$$\sigma_t = [3\sigma^2 + (0.001r)^2 + \Delta^2]^{1/2}$$

where σ is the standard deviation from the least-squares refinement, r is the parameter and Δ is the maximum difference between parameters obtained in the three different refinement schemes (cf. Table 2).

TABLE 2
MOLECULAR PARAMETERS OF $\text{CH}_2\text{ClSiCl}_3$

Independent parameters	Molecular symmetry		
	C_s	C_s	C_1
Si—Cl(pm)	202.69(3)	202.65(4)	202.67(4)
Si—C(pm)	184.9(5)	184.7(6)	184.4(6)
C—Cl(pm)	179.2(5)	178.4(5)	179.0(5)
C—H(pm)	110.8(10)	110.6(18)	111.1(10)
Cl2...Cl4(pm)	362.9(8)		
Cl2...Cl4(pm)	476.2(4)		
Cl2...H5(pm)	406.8(3)		
Cl1—Si—C($^\circ$)	109.66(6)	109.55(7)	106.69(7)
Si—C—Cl4($^\circ$)	111.3(2)	111.3(2)	111.4(2)
Cl—Si—C—Cl($^\circ$)	0	0	10.4(6)

r_a values with their standard deviations parenthesized

TABLE 3
GAS-PHASE MOLECULAR GEOMETRY OF CH₂ClSiCl₃

Bond lengths ^a	r_g (pm)
Si—Cl	202.8(2)
Si—C	185.1(10)
C—Cl	179.4(11)
C—H	111.2(18)
Bond angles	r_α (°)
Si—C—Cl	111.7(4)
Cl—Si—C	109.95(21)

Spectroscopic calculations

Mean parallel amplitudes of vibrations (l) and perpendicular corrections ($K = \langle (\Delta x)^2 + (\Delta y)^2 \rangle / 2r$) have been calculated for (chloromethyl)trichlorosilane. An approximate force field was compiled and adjusted to the experimental frequencies of Table 1. The calculated quantities are given in Table 4. There is a fairly good agreement between the l values determined from electron diffraction (also given in Table 4) and those from the calculations. The experimental l values and calculated K values were employed to produce the r_α average bond angles given in Table 3 from the r_a distances determined from electron diffraction.

Barrier to internal rotation

The barrier to internal rotation around the Si—C bond was estimated to be

TABLE 4
VIBRATIONAL PARAMETERS OF CH₂ClSiCl₃

	l (pm) [309 K]		K (pm) [309 K]
	Electron diffraction experimental	Spectroscopic calculation	
Si—Cl	4.65(14)	4.90	0.72
Si—C	6.7	5.91	0.36
C—Cl	6.0(5)	5.70	1.47
C—H	6.4(19)	7.83	1.91
Cl4...H5	18.4	11.65	1.96
Si...H5	19.9 (35)	11.82	1.08
Si...Cl4	7.9(5)	12.58	0.85
Cl1...Cl2	8.6	10.30	0.76
C...Cl1	8.6	12.75	0.32
Cl1...H5	20.0(5)	19.78	0.75
Cl3...H5	20.0	19.48	0.94
Cl2...Cl4(gauche)	21.3(10)	25.10	0.49
Cl1...Cl4(anti)	9.0(5)	13.64	0.28
Cl2...H5	9.6(45)	12.75	0.80
H5...H6	13.5(assumed)	15.66	2.02

The parenthesized values are estimated errors (σ_t) obtained from the formula $\sigma_t = [\sigma^2 + (0.02l)^2]^{1/2}$ where σ is the standard deviation from the least-squares refinement.

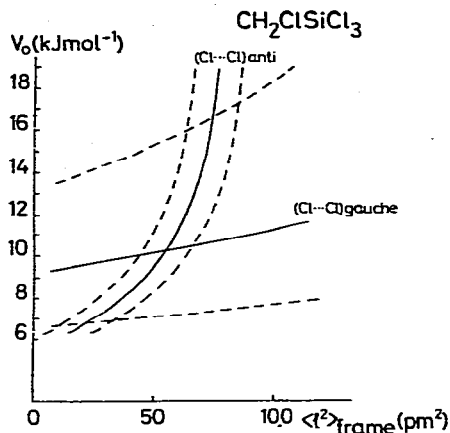


Fig. 4. Graphical determination of the barrier to internal rotation according to ref. 12.

between 7 and 17 kJ mol⁻¹ by Karle's method [12]. This estimation is illustrated in Fig. 4. From the average rotational angle determined in one of the refinements (10°, see Table 2) a very similar barrier could be expected from Vilkov et al.'s method [13].

Discussion

The Si-Cl and Si-C bond lengths in CH₂ClSiCl₃ are the same as those in methyltrichlorosilane [14]: $r_s(\text{Si-Cl})$ 202.6 pm and $r_s(\text{Si-C})$ 184.8 pm. The silicon bond angles also agree well within the estimated error limits. Thus the substitution of one of the methyl hydrogens by chlorine causes no appreciable structural changes in the rest of the molecule. The C-Cl bond length of CH₂ClSiCl₃ is also very similar to that of CH₃CH₂Cl (r_s 178.8 ± 0.2 pm) [15].

The conformation of (chloromethyl)trichlorosilane is unambiguously staggered. The estimated barrier to internal rotation is listed in Table 5 along with those of related molecules with silicon-carbon central bonds. Some estimated Van der Waals energies are also given. The Van der Waals contribution becomes

TABLE 5
BARRIERS TO INTERNAL ROTATION (V_0) AND CALCULATED VAN DER WAALS ENERGIES (V_{vdw})

Compound	V_0 (kJ mol ⁻¹)	V_{vdw} (kJ mol ⁻¹)
CH ₃ -SiH ₃	7.1 [16]	0 ^a
CH ₂ Cl-SiH ₃	10.7 [17]	0.08 ^a
CH ₃ -SiCl ₃		0.10 ^b
CH ₂ Cl-SiCl ₃	10.3	2.49 ^a
CHCl ₂ -SiCl ₃		5.04 ^c
CCl ₃ -SiCl ₃	16.3 [18]	8.45 ^a

^a Calculated from known molecular parameters. ^b Calculation based partly on geometry assumed from the other molecules. ^c Calculation based on assumed molecular geometry.

appreciable only when chlorine atoms appear on both ends of the central bond. Also, as expected, V_{vdw} increases rather evenly with the increasing number of Cl...Cl interactions. As the V_0 and V_{vdw} values of $CH_2Cl-SiCl_3$ and CCl_3-SiCl_3 are compared, it is seen that the contributions to the total barrier from sources other than Van der Waals interaction remain constant as the number of Cl...Cl interactions is increased.

Acknowledgements

Experimental work by Mrs. Mária Kolonits and technical assistance by Mrs. Mária Csányi are gratefully acknowledged.

Notes added in proof

(1) After submitting this paper we learned from Drs. M. Dakkouri and V. Typke (Ulm) that a similar investigation was being completed in their laboratory.

(2) Additional calculations allowing also a tilt of the $SiCl_3$ group resulted in changes of the parameters for the C_1 model within the error limits and a small tilt angle barely larger than its standard deviation.

References

- 1 I. Hargittai and B. Rozsondai, *Kém. Közlem.*, **50** (1978) 427.
- 2 K. Sera, K. Suehiro, M. Hayashi and H. Murata, *Bull. Chem. Soc. Japan*, **49** (1976) 29.
- 3 V.A. Svyatkin, A.K. Maltsev and O.M. Nefedov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **26** (1977) 1071.
- 4 L.M. Sverdlov, M.A. Kovner and E.P. Krainov, *Vibrational Spectra of Molecules*, Nauka, Moscow, 1970, (in Russian).
- 5 K. Ohno and H. Murata, *Bull. Chem. Soc. Japan*, **45** (1972) 3333.
- 6 J.H. Schachtschneider, *Tech. Rept. 231-64*, Shell Development Company, Emeryville, California, USA (1964).
- 7 I. Hargittai, J. Hernádi, M. Kolonits and Gy. Schultz, *Rev. Sci. Instrum.*, **42** (1971) 546.
- 8 I. Hargittai, J. Hernádi and M. Kolonits, *Prib. Tekh. Eksp.*, (1972) 239.
- 9 J. Tremmel, M. Kolonits and I. Hargittai, *J. Phys. E.: Sci. Instrum.*, **10** (1977) 664.
- 10 M. Hargittai and I. Hargittai, *J. Chem. Phys.*, **59** (1973) 2513.
- 11 B. Andersen, H.M. Seip, T.G. Strand and R. Stølevik, *Acta Chem. Scand.*, **23** (1969) 3224.
- 12 J. Karle, *J. Chem. Phys.*, **45** (1966) 4149.
- 13 L.V. Vilkov, N.P. Penionzhkevich, J. Brunvoll and I. Hargittai, *J. Mol. Struct.*, **43** (1978) 109.
- 14 H. Takeo and C. Matsumura, *Bull. Chem. Soc. Japan*, **50** (1977) 1633.
- 15 R.H. Schwendeman and G.D. Jacobs, *J. Chem. Phys.*, **36** (1962) 1245.
- 16 R.W. Kilb and L. Pierce, *J. Chem. Phys.*, **27** (1957) 108.
- 17 R.H. Schwendeman and G.D. Jacobs, *J. Chem. Phys.*, **36** (1962) 1251.
- 18 Y. Morino and E. Hirota, *J. Chem. Phys.*, **28** (1958) 185.