Synthesis and Characterization of $Cl_2HSi\text{-}O\text{-}NMe_2$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

O-(Dichlorosilyl)-*N,N*-dimethylhydroxylamine, $Cl_2HSiONMe_2$, was synthesised by the reaction of *O*-lithio-*N,N*-dimethylhydroxylamine with an excess of trichlorosilane. The compound was characterised by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{15}N, ^{29}Si), gas-phase IR spectroscopy and mass spectrometry. The structure of $Cl_2HSiONMe_2$ was determined by gas-phase electron diffraction. It exists as two conformers in the vapour, named *anti* and *gauche* after the position of the SiH hydrogen atom relative to the SiON skeleton. The *anti*:*gauche* ratio in the vapour was determined to be 40:60. The *anti* conformer shows only a weak attractive interaction between the geminal donor and acceptor centres N and Si [angle Si-O-N 111.1(20)°], whereas these interactions are stronger in the *gauche* conformer [angle Si-O-N 98.8(12)°]. Further structure-determining forces from weak hydrogen bridges of the Si-Cl···H-C type and van der Waals repulsive forces are also discussed. The experimental results are in reasonable agreement with *ab initio* calculations at the MP2/6-311++G** level of theory.

Key words: Silicon, Hydroxylamine, Donor Bonds, Electron Diffraction

Introduction

In contrast to carbon, silicon compounds with co-ordination numbers of higher than four are easily accessible [1]. Such compounds are known since the the beginning og the nineteenth century, when the formation of the adduct $SiF_4 \cdot 2\ NH_3$ was reported [2, 3]. In recent years important findings on very high coordination numbers were made, in particular *CN* = 7 [4, 5] and CN = 8, which was established in bis-1-[2,6-bis(dimethylaminomethyl)phenyl]silane (Si···N contacts), [6] $[C_6H_2(CF_3)_2]_2SiF_2$ (Si···F contacts) [7] and $Si(ONMe_2)_4$ (Si···N contacts). [8] The enhanced reactivity of hypoercoordinate silicon compounds has been discussed in detail in reviews by Holmes [9] and Chuit *et al.* [10].

Within the class of intramolecularly hypercoordinate silicon compounds, those which have only one atom between silicon and the donor centre are a special case. Structure-determining interactions between geminal donor and acceptor atoms in main group compounds are a widely found phenomenon, which is still poorly understood in terms of the description of chemical bonding. In this context *O*-silylhydroxylamines, *i.e.* compounds containing Si-O-N backbones, have been investigated in quite some detail. *O*-Silylhydroxylamines containing electronegative substituents such as halogen atoms bonded to the silicon atom show relatively strong intramolecular interactions between silicon and nitrogen atoms. One of the strongest interactions so far was observed in $F_3SiONMe_2$ [11], which has an Si-O-N angle of 77.4(1)° and an Si···N distance of 1.963(1) Å in the solid state. In the gas phase the values for these parameters [94.3(9)°, 2.273(17) Å] indicate a much weaker interaction and thus a marked dependence of the molecular structure on the polarity and/or polarizability of the surrounding medium.

Replacement of the fluorine by chlorine substituents leads to a much weaker interaction between silicon and nitrogen atoms, as could be shown in $Cl_3SiONMe_2$ [12], which has an Si-O-N angle of 103.1(1)° and an Si···N distance of 2.437(1) Å in the crystalline phase and only slightly different values in the gas phase [105.6(8)°, 2.473(12) Å]. It seems that in this case the steric demand of three chlorine substituents makes it more difficult to enlarge the coordi-
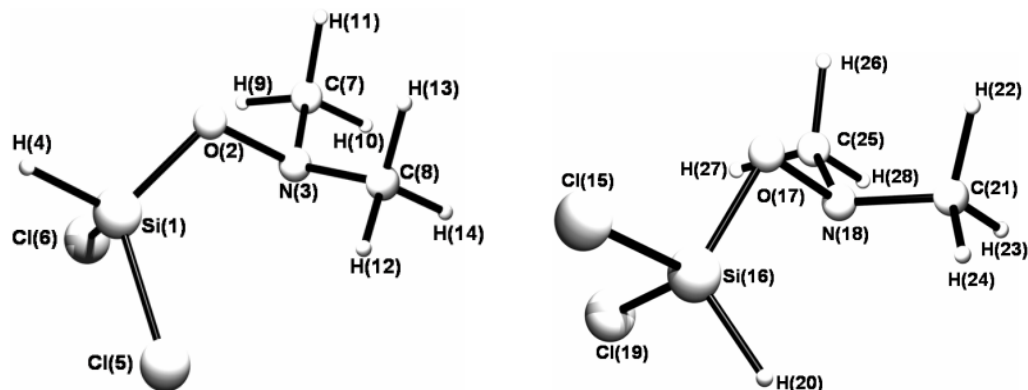
Fig. 1. Molecular structures of the *anti* (left) and the *gauche* (right) conformers of Cl$_2$HSiONMe$_2$ as determined by electron diffraction in the gas phase.

Table 1. Theoretical and GED data for the combined refinement of the *gauche* and *anti* conformers of Cl$_2$HSiONMe$_2$.

Parameter (r in Å, $\angle$ in °)	*gauche* Conformer		*anti* Conformer	
	GED	MP2/ 6-311++G**	GED	MP2/ 6-311++G**
rSiCl	2.024(11)	2.039[a]	2.040(5)	2.039[a]
rSiH	1.462(8)	1.458	1.460(5)	1.459
rSiO	1.643(7)	1.664	1.644(4)	1.658
rON	1.475(13)	1.468	1.471(10)	1.465
rNC	1.451(7)	1.458[a]	1.451(7)	1.458[a]
rCH	1.097(4)	1.094[a]	1.097(4)	1.094[a]
$\angle$OSiH	113.5(10)	113.3	106.1(10)	106.0
$\angle$OSiCl	101.9(8)[b]	104.7[b]	111.8(5)	111.5[b]
	111.8(5)[c]	111.6[c]		
$\angle$SiON	98.8(12)	99.3	111.1(20)	105.5
$\angle$ONC	107.2(4)	105.6[a]	107.0(4)	105.3[a]
$\angle$NCH	109.0(5)	109.4[a]	109.0(5)	109.4[a]
$\angle$Cl$_{eq}$SiON[1]	68.6(13)		59.8(24)	61.1
$\angle$Cl$_{ax}$SiON	175.4(17)	174.7		
$\angle$SiONC[1]	115.9(8)	121.0	115.9(8)	121.3
$\angle$ONCH$_f$[1]	64.0(41)	63.3	64.0(41)	63.5

[1] Only the absolute value is considered; [a] average value from *ab initio* calculations; [b] atom is in *gauche* position; [c] atom is in *anti* position; [f] atom is facing toward silicon; [ax] atom is in axial position; [eq] atom is in equatorial position.

nation sphere of silicon and thus lead to a strong attractive Si$\cdots$N interaction. Consequently, the structure of the Si-O-N skeleton based on a weak Si$\cdots$N interaction is less dependent on the medium.

Surprisingly and despite the presence of less electronegative substituents at silicon, ClH$_2$SiONMe$_2$ shows a much stronger Si$\cdots$N interaction than the trichloro compound Cl$_3$SiONMe$_2$, as deduced from an SiON angle in the solid state [79.7(1)°] [13] comparable to that for F$_3$SiONMe$_2$. However, there are two structurally very different conformers present in the gas phase of ClH$_2$SiONMe$_2$. The one that has the chlo-

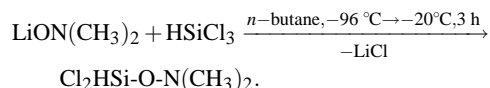rine atom in the *anti* position relative to the SiON backbone has a much stronger Si$\cdots$N interaction [$\langle$SiON$_{anti}$ 87.1(9)°] than the conformer with chlorine adopting the *gauche* position [$\langle$SiON$_{gauche}$ 104.7(11)°]. This shows that it is mainly the electronegativity of the *anti*-positioned substituent that determines the strength of the Si$\cdots$N interaction, as the *gauche* conformer, which bears an H atom in the position *anti* to N, behaves structurally very much like the completely hydrogenated system H$_3$SiONMe$_2$ [$\langle$SiON 102.6(1)°, in the crystal] [14].

In order to prove this empirical concept it seemed desirable to complete the series of Si-chlorinated silylhydroxylamines. In this contribution we report on the synthesis of Cl$_2$HSiONMe$_2$, its structure determination in the gas phase and a comparison of these data to the available sets for Cl$_3$SiONMe$_2$ and ClH$_2$SiONMe$_2$.

Results

Synthesis and characterization of Cl$_2$HSi-O-NMe$_2$

The compound was prepared by the reaction of LiONMe$_2$ with an excess of HSiCl$_3$ in *n*-butane as a solvent. Under these conditions it is possible to obtain the compound in 27% yield after purification by fractional condensation. If the reaction is conducted at 0 °C in diethyl ether and under stoichiometric conditions, HSi(ONMe$_2$)$_3$ is formed in 64% yield [15].

$$\text{LiON(CH}_3)_2 + \text{HSiCl}_3 \xrightarrow[-\text{LiCl}]{n-\text{butane},-96\,°C \rightarrow -20°C, 3\,h}$$
$$\text{Cl}_2\text{HSi-O-N(CH}_3)_2.$$

At ambient temperature the compound is a colourless liquid, which solidifies as a glassy material at low
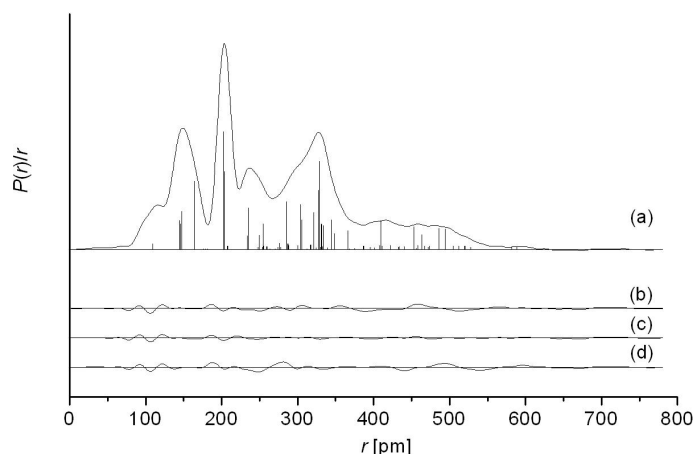
Fig. 2. Molecular scattering intensity curves for Cl$_2$SiONMe$_2$ as obtained by gas electron diffraction.

Table 2. Parameter descriptions for the least-squares refinement of the gas-phase electron-diffraction data for Cl$_2$HSiONMe$_2$. Restraints as used in the SARACEN method of data refinement are provided in the last column.

Parameter	Description	Value	Restraint
p_1	rSiO	1.644(4)	1.644(10)
p_2	rSiH	1.460(5)	1.460(5)
p_3	rSiCl	2.040(5)	2.040(5)
p_4	rCH	1.097(4)	1.097(5)
p_5	rNC	1.451(7)	
p_6	rON	1.471(10)	1.471(10)
p_7	∠O(2)-Si(1)-H(4)	106.1(10)	106.1(10)
p_8	∠O(2)-Si(1)-Cl(5/6)	111.8(5)	
p_9	∠Si(1)-O(2)-N(3)	111.1(21)	
p_{10}	∠O(2)-N(3)-C(7/8)	106.7(4)	
p_{11}	∠N(3)-C(7/8)-H	109.0(5)	109.0(5)
p_{12}	τSi(1)-O(2)-N(3)-C(7/8)	115.9(8)	
p_{13}	τO(2)-N(3)-C(7/8)-H$_f$	64.0(41)	64.0(50)
p_{14}	τCl(5/6)-Si(1)-O(2)-N(3)	59.8(24)	
p_{15}	rSiO_diff	−0.000(5)	0.000(5)
p_{16}	rSiH_diff	0.001(5)	
p_{17}	rSiCl_diff	−0.015(9)	
p_{18}	rON_diff	0.004(5)	0.004(5)
p_{19}	∠O(17)-Si(16)-H(20)	113.5(10)	113.5(10)
p_{20}	∠O(17)-Si(16)-Cl(15)	101.9(8)	
p_{21}	∠Si(16)-O(17)-N(18)	98.8(13)	
p_{22}	τCl(15)- Si(16)-O(17)-N(18)	175.4(17)	
p_{23}	τCl-Si-O-Cl	106.8(8)	106.8(10)
p_{24}	x_{anti}	0.400	

temperatures. Consequently, we were so far not able to obtain single crystals of the compound.

Cl$_2$HSiONMe$_2$ was characterised by NMR and IR spectroscopy and by mass spectrometry. As expected, the compound shows two singlets in the ^{1}H NMR spectrum at 2.13 and 5.43 ppm, the latter with ^{29}Si satellites. The ^{15}N NMR chemical shift (−239.5 ppm) is the lowest in the series Cl$_x$H$_{3-x}$SiONMe$_2$ including H$_3$SiONMe$_2$ (−234.0 ppm), ClH$_2$SiONMe$_2$ (−228.9 ppm) and Cl$_3$SiON(CH$_3$)$_2$ (−229.4 ppm). There is also no linear relationship between the degree of chlorination and the ^{29}Si NMR chemical shift as is indicated by the series H$_3$SiONMe$_2$ −49.5, ClH$_2$SiONMe$_2$ −54.6, ClH$_2$SiONMe$_2$ −46.7 and Cl$_3$SiONMe$_2$ −42.4 ppm], in which ClH$_2$SiONMe$_2$ describes the minimum. The value of the coupling constant ^1J(SiH) and the Si-H bond stretching frequency in the infrared spectra reflect the strengthening of the Si-H bond in the series H$_3$SiONMe$_2$ [^1J(SiH) 219.3 Hz, ν(SiH) 2177 cm^{-1}], ClH$_2$Si-O-NMe$_2$ [^1J(SiH) 287.0 Hz, ν(SiH) 2218 cm^{-1}] and ClH$_2$SiONMe$_2$ [^1J(SiH) 336.9 Hz, ν(SiH) 2253 cm^{-1}].

Gas-phase structure

Due to the infeasibility of a crystal structure determination the only experimental access to a molecular structure is by gas-phase electron diffraction. We have undertaken such an experiment facing the problems involved with the simultaneous presence of two conformers. On the other hand this allowed us to retrieve information for both conformers from experimental data, which is important in the light of having shown in the past that SiON systems are in particular difficult to predict reliably by medium level *ab initio* calculations [11, 16]. Employing large basis sets and high levels of electron correlation treatment (*e. g.* coupled cluster methods) is, however, not feasible for molecules of this size.

The highest level *ab intio* calculations we ran for Cl$_2$HSiONMe$_2$ were of the MP2/6-311++G** quality. These data predicted the energy difference between
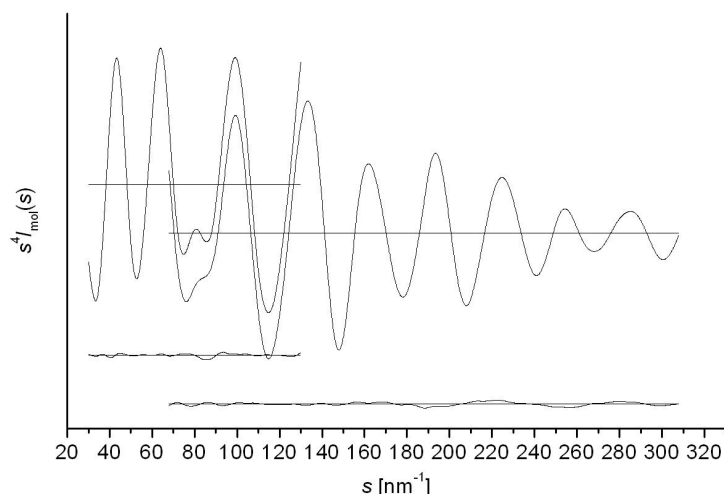
Fig. 3. Radial distribution curves for $Cl_2SiONMe_2$ as obtained by gas electron diffraction. (a) Final experimental curve with 40% *anti* and 60% *gauche* conformer, (b) difference curve observed for the *anti* conformer only, (c) difference curve observed for both conformers with a 40% : 60% ratio (*anti* : *gauche*), and (d) difference curve observed for the *gauche* conformer only. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/[(Z_{Cl}-f_{Cl})(Z_{Si}-f_{Si})]$.

the *gauche* and the *anti* conformers to be 0.7 kJ mol^{-1} ($E_g - E_a$), *i.e.* the *gauche* conformer is slightly lower in energy than the *anti* conformer. Subsequent evaluations of refinements with different conformer ratios employing the 95% confidence limit showed that a contribution of 40% *anti* conformer in the vapour describes the situation best and therefore agreed very well with the energy difference established from the *ab initio* calculations. The final refinements were thus undertaken with this ratio being fixed.

Several further assumptions had to be made to restrict the number of refining parameters to a tractable quantity. The values of C-H and N-C bond lengths, and those of ONC, NCH and CNC bond angles (*via* the respective dihedral angles) were set the same for both conformers. In addition it was decided to define the NCH bond angle *via* internal HCH angles of the methyl groups even though the *anti* conformer is of higher symmetry (C_s instead of C_1 for the *gauche* conformer). Within the same conformer, the lengths of both Si-Cl distances were refined with a common value. For the OSiCl angles it was assumed that both are equal within each conformer. Parameters present in both conformers were defined as parameters for the *anti*-conformer, whereas for the *gauche* conformer the corresponding parameters were defined by differences to the *anti* parameters. Several of these parameters were subject to flexible restraints in the refinements, according to the SARACEN procedure [17,18]. A list of these restraints is provided in Table 3.

The program SHRINK [9] was used to extract values for amplitudes of vibration and the curvilinear corrections of *k*-values for all individual atom pairs of

Table 3. Details of the GED experiment. Numbers in parentheses are estimated standard deviations of the last digit.

d [mm]	Weighting functions [nm^{-1}]					q	k	λ [pm]	R_g	R_d
	Δs	s_{min}	sw_1	sw_2	s_{max}					
128.19	4.00	68	88	264	308	0.4284	1.697(35)	6.02	7.04 %	6.22%
286.03	2.00	30	50	112	130	0.4473	1.697(14)	6.02	6.10%	4.16%

the respective conformers from data calculated at the B3PW91/6-311++G** level for the experimental temperature settings.

The *anti* and *gauche* conformers of $Cl_2HSiONMe_2$ are quite different with regard to the structures of their SiON backbones. The *gauche* conformer has an Si-O-N angle of 98.8(12)°, which is therefore more than 12° narrower than the corresponding angle in the *anti* conformer. This reflects the different nature of the silicon substituents in the *anti* position relative to the nitrogen atom, which is the electronegative Cl substituent in the *gauche* conformer, but the much less electronegative H substituent in the *anti* conformer. However, it is not only electronic arguments that can be used to explain the differences, but also steric ones. The two chlorine atoms in the *anti* conformer come close to the hydrogen atoms of the methyl groups at nitrogen. The closest Cl$\cdots$H distances are 2.88 Å, which is substantially less than the sum of established van der Waals radii (3.01 Å) [20]. Arguing purely with repulsive forces in this context might be misleading, as in the last years a number of M-Cl$\cdots$H-C hydrogen bonds have also been recognised as such [21] and such an attractive contribution cannot be ruled out in our case. There is no possibility for the *anti* con-

former to distort its geometry in such a way that it can optimise the attractive $Si \cdots N$ interaction, because changing the torsion angle NOSiH in order to find a conformation where one of the chlorine atoms comes approximately into a position *cis* relative to nitrogen and thus adopts comparable distances to both methyl groups, would lead to a loss of $Si \cdots N$ attractive interaction.

In the *gauche* conformer there is only one such close contact between a chlorine atom and a methyl group, characterised by a shortest $Cl \cdots H$ distance of 2.87 Å, which is very similar to the corresponding value in the *anti* conformer. The similarity of these non-bonded $Cl \cdots H$ distances suggests that this seems to be the equilibrium distance defined by steric repulsion and attraction through weak hydrogen bonding. By slight variation of the torsion angles ClSiON [68.6(13)°] and 175.4(17)°] from the idealised values (60 and 180°) a maximum in attractive $Si \cdots N$ potential energy gain is balanced with the $Cl \cdots H$-C interaction.

The O-Si-Cl angles were calculated to be markedly different for the *anti* and *gauche* Cl positions in the *gauche* conformer, but almost identical for *gauche* positions in the two conformers. In the refinements it was therefore assumed that there were just two independent angles, refining to 111.8(5)° for the *trans* conformer and 101.9(8)° and 111.8(5)° for the *gauche* form. In the *gauche* conformer this reflects a marked distortion of the coordination geometry at silicon away from a tetrahedral environment.

The shortest distance between the silicon-bound hydrogen atom and a hydrogen atom of the methyl groups is 2.70 Å and therefore much wider than twice the van der Waals radius of hydrogen, which is 2.4 Å.

In earlier contributions the N-O bond lengths have been found to scatter over a range between 1.47 and 1.51 Å {all crystal structure values: H₃SiONMe₂ 1.471 Å [14], Cl₃SiONMe₂ 1.492(av) Å [16], ClH₂SiONMe₂ 1.490(1) Å [12], F₃SiONMe₂ 1.508(1) Å [11]}, with the largest value found for F₃Si ONMe₂, the compound with the most pronounced $Si \cdots N$ interaction. The values of 1.475(13) (*gauche*) and 1.470(10) Å (*anti*) for Cl₂HSiONMe₂ are thus at the lower end of the range established for SiON compounds.

Most of the other geometric parameters defining the structures of the two conformers of Cl₂HSiONMe₂ are typical for such compounds and deserve no further comments.

Table 4. Selected distances (pm), amplitudes of vibration (pm) and *k*-values, including the selected tying scheme, for the refinement of the gas-phase electron-diffraction data for Cl₂HSiONMe₂.

Amplitude	Description	Distance	*u*-Value	Tied to	*k*-Value
u_1	Si1-O2	164.2(4)	6.4	u_{93}	0.13
u_2	Si1-H4	145.9(5)	8.7	u_{95}	0.37
u_3	Si1-Cl5	203.9(5)	5.0	u_{92}	0.09
u_5	O2-N3	146.1(5)	4.9	u_{96}	0.22
u_9	C7-H10	109.6(4)	7.7(4)		0.38
u_{14}	Si1$\cdots$N3	254.4(32)	11.1	u_{117}	−1.27
u_{15}	Si1$\cdots$C7	348.0(27)	11.2	u_{122}	−1.84
u_{25}	O2$\cdots$Cl6	305.3(8)	9.3(6)		−0.18
u_{26}	O2$\cdots$C7	234.0(8)	6.0	u_{132}	0.13
u_{35}	N3$\cdots$Cl5	334.4(36)	26.6	u_{136}	−1.27
u_{53}	Cl5$\cdots$Cl6	326.9(83)	8.1	u_{107}	−0.25
u_{54}	Cl5$\cdots$C7	463.2(33)	29.3	u_{149}	−3.44
u_{55}	Cl5$\cdots$C8	365.8(47)	38.3	u_{149}	−1.36
u_{70}	C7$\cdots$C8	249.5(16)	7.1	u_{161}	0.01
u_{92}	Cl15-Si16	202.5(4)	5.0(2)		0.14
u_{93}	Si16-O17	164.2(4)	6.4(4)		0.12
u_{94}	Si16-Cl19	202.4(4)	5.1	u_{92}	0.09
u_{95}	Si16-H20	145.7(7)	8.7(9)		0.35
u_{96}	O17-N18	147.6(11)	4.8(5)		0.19
u_{98}	N18-C25	144.8(7)	8.1(7)		0.12
u_{105}	Cl15$\cdots$O17	285.4(16)	7.8	u_{107}	−0.18
u_{106}	Cl15$\cdots$N18	409.8(13)	14.2	u_{136}	−2.36
u_{107}	Cl15$\cdots$Cl19	328.5(56)	8.2(7)		−0.41
u_{109}	Cl15$\cdots$C21	485.9(16)	22.1	u_{149}	−3.14
u_{113}	Cl15$\cdots$C25	494.5(22)	18.9	u_{149}	−2.80
u_{117}	Si16$\cdots$N18	234.8(20)	14.3(12)		−1.45
u_{118}	Si16$\cdots$C21	331.1(17)	14.3	u_{122}	−2.36
u_{122}	Si16$\cdots$C25	331.8(17)	11.7(23)		−1.87
u_{126}	O17$\cdots$Cl19	304.0(8)	7.6	u_{107}	−0.19
u_{132}	O17$\cdots$C25	235.2	6.1(5)		0.13
u_{136}	N18$\cdots$Cl19	321.2	26.1(24)		−1.26
u_{145}	Cl19$\cdots$C21	453.1	29.0	u_{149}	−3.28
u_{149}	Cl19$\cdots$C25	344.8	36.1(26)		−1.52
u_{161}	C21$\cdots$C25	249.5	7.1(7)		0.06

Conclusion

The structures of the two conformers of Cl₂HSiO NMe₂ show that different structure-determining forces are operative in this compound. The generally shallow bending potentials of silylated oxygen compounds allow other weak interactions, such as the attractive geminal donor-acceptor interaction ($Si \cdots N$) but also repulsive van der Waals and attractive weak hydrogen-bond interactions, to become dominant forces determining the molecular structure of such Si-O compounds.

Experimental Section

Preparation. A solution of *n*-butyllithium (9.0 ml of a 1.6 molar solution in *n*-hexane, 14 mmol) was added dropwise to a solution of *N,N*-dimethylhydroxylamine (1.1 ml, 0.9 g, 15 mmol) in *n*-pentane (20 ml) at −78 °C. After complete

Table 5. Correlation matrix elements with absolute values greater than 50 for the least-squares refinement of the gas-phase electron-diffraction data for Cl$_2$HSiONMe$_2$.

	p_{14}	p_{15}	p_{17}	p_{20}	p_{21}	p_{22}	u_{98}	u_{107}	u_{122}
p_1		−61							
p_3			−99						
p_6							−50		
p_8				77		−51			
p_9	−53				−66	−56			−70
p_{14}						93		90	
p_{20}						−51			
p_{22}								91	
u_{93}							53		

addition of the *n*-butyllithium solution the reaction mixture was allowed to warm slowly to room temperature while stirring for 1 h. The solvents were removed *in vacuo* to leave a residue of LiONMe$_2$. 15 ml of *n*-butane were condensed onto this LiONMe$_2$ followed by HSiCl$_3$ (3.0 ml, 4.1 g, 30 mmol) at −196 °C. The reaction mixture was warmed to −96 °C by immersion in a toluene slush and then over a period of several hours to −20 °C. The mixture was stirred at this temperature for 3 h. All volatile compounds were condensed into a cold trap. This mixture of volatile compounds was carefully warmed to room temperature and the *n*-butane was evaporated through a bubbler valve. Unreacted HSiCl$_3$ was removed by distillation at 45 °C. The remaining colourless liquid was identified as pure Cl$_2$HSiONMe$_2$, yield 0.60 g (3.9 mmol, 27%).

NMR spectra were recorded in pre-dried C$_6$D$_6$ (K/Na alloy) on an AMX400 Bruker NMR spectrometer. ^{1}H NMR $\delta = 2.13$, (s, 6H, CH$_3$), $\delta = 5.43$ (s, 1H, SiH). – ^{13}C NMR $\delta = 48.1$ (qq, $^1J_{CH} = 137.3$ Hz, $^3J_{CNCH} = 4.8$ Hz). – ^{15}N{^{1}H} NMR $\delta = -239.5$ (s). – ^{29}Si NMR $\delta = -46.7$ (d, $^1J_{SiH} = 336.9$ Hz). A gas-phase infrared spectrum was recorded on a Midac Prospect IR-spectrometer: IR (gas) $v = 3009$ (m), 2977 (m), 2912 (m), 2884 (m, vCH), 2253 (s, vSiH), 1474 (w), 1449 (w), 953 (m), 911 (vs), 851 (m), 818 (vs), 764 (m), 585 (vs) cm^{-1}. A GC-coupled mass spectrum was recorded on an HP 5890 series II mass spectrometer: GC-MS(EI): *m/z* = 160 (M$^+$), 116 [M$^+$ - N(CH$_3$)$_2$].

Ab initio calculations. The *ab initio* and hybrid DFT calculations were performed with the Gaussian98 suite of programs [22] with the methods and basis sets implemented therein. Both the geometry and the frequencies of the *gauche* and *anti* conformers of HSiCl$_2$ONMe$_2$ were calculated and further used for calculations of vibrational amplitudes.

Gas-phase electron diffraction. Electron-diffraction data were collected on Kodak Electron Image photographic films using the Edinburgh gas-phase electron-diffraction apparatus [23]. The sample temperature of Cl$_2$HSiONMe$_2$ was maintained at 279 K and that of the nozzle at 293 K to prevent sample condensation in the nozzle. Films were exposed at two different camera distances. The acceleration voltage was set to 40 kV, resulting in an electron wavelength of *ca.* 6 pm. Precise camera distances (*d*) and electron wavelengths (λ) were determined by analysis of the scattering pattern of benzene, recorded immediately before or after the sample patterns. Details of weighting functions, *s*-ranges, scale factors (*k*) [24] and correlation parameters (*q*) are summarised in Table 3, selected interatomic distances and vibrational amplitudes in Table 4 and the final least-squares correlation matrix in Table 5. The scattering intensities were measured using an Epson Expression 1600 Pro flatbed scanner and corrected to mean optical densities as a function of the scattering variable, *s*, using an established program [25]. The data for the studied compound were reduced and analysed using the ed@ed [26] program with the scattering factors of Ross *et al.* [27].

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