

The Molecular Structure of Bis(chloromethyl) Ether, $\text{ClH}_2\text{C}-\text{O}-\text{CH}_2\text{Cl}$, in the Gas Phase

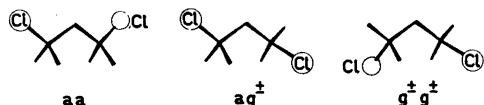
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The structure of bis(chloromethyl) ether has been studied by the electron diffraction method in the vapour phase. Both chlorine atoms are found to have the same *gauche* relation (g^+g^+ or g^-g^-) to the COC chain, the dihedral angles $\delta(\text{ClCOC})$ being 69.6° . The following structure parameters have been determined: $r(\text{C}-\text{O})=1.393(3)$ Å, $r(\text{C}-\text{Cl})=1.800(3)$ Å, $r(\text{C}-\text{H})=1.100(12)$ Å, $\angle\text{COC}=114.2(1.5)^\circ$, $\angle\text{OCCl}=112.2(0.8)^\circ$, $\angle\text{OCH}=111.6(2.2)^\circ$.

This electron diffraction investigation of bis(chloromethyl) ether (Fig. 1) is part of a study of the structures of cyclic and acyclic ethers.

Molecules of the type $\text{XCH}_2-\text{O}-\text{CH}_2\text{X}$ may have four distinguishable conformers: *aa*, *ag*, $g^\pm g^\pm$, and g^+g^- . Of these the g^+g^- conformer may be disregarded because of the short $\text{Cl}\cdots\text{Cl}$ distance. The three different conformations which may be present in the gas phase are therefore the following for bis(chloromethyl) ether:



The conformational problem of this molecule has been investigated earlier by dipole moment investigations in the gas phase¹ and in non-

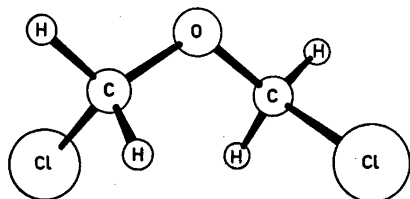


Fig. 1. Bis(chloromethyl) ether.

polar solution,² and by Raman³ and infrared⁴ spectroscopy. The conclusion obtained from these methods is that the molecule has a shallow minimum about its equilibrium position, which suggests a distribution of slightly different conformers to be present. Chiba¹ has found, based on temperature dependent dipole moment measurements, that the $g^\pm g^\pm$ conformer possesses the lowest energy, determined to be 1.3 kcal below the *ag* conformation.⁵

EXPERIMENTAL

A commercial sample of bis(chloromethyl) ether was obtained from Fluka. The electron diffraction diagrams were taken on a Balzer Eldigraph KDG2. The sample temperature was kept at about 10°C during the exposures, and the pressure in the apparatus was approximately 1×10^{-6} Torr. The diffraction diagrams were recorded at 25.00 and 50.00 cm nozzle-to-plate distances, the electron wavelengths being 0.05852 and 0.05847 Å, respectively. Five selected plates were analysed for each nozzle-to-plate distance. The intensities were modified by $s/|f_C||f_O|$, where $|f|$ is the scattering amplitude^{6,7} for carbon and oxygen.

The experimental data were analysed in the usual way.⁸ The experimental data obtained cover scattering angles corresponding to an s -range of $1.75-29.75$ Å⁻¹. The molecular intensity curve is shown in Fig. 2. A least-squares procedure was used to refine the distances and vibrational amplitudes estimated from the experimental radial distribution (RD) curve.

The calculations have been carried out on CDC 3300 and CDC 7400 (CYBER) computers.⁸

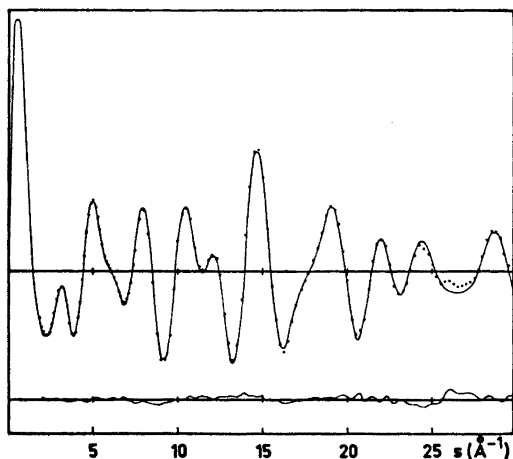


Fig. 2. Bis(chloromethyl) ether. Theoretical molecular intensity curve. The dots show the experimental values. The lower curve shows the difference between the experimental and theoretical values.

STRUCTURE ANALYSIS AND RESULTS

Approximate values for the parameters used in the least-squares analysis are determined from the experimental RD curve on Fig. 3.

The three first well separated peaks in the RD curve at about 1.1, 1.4, and 1.8 Å corre-

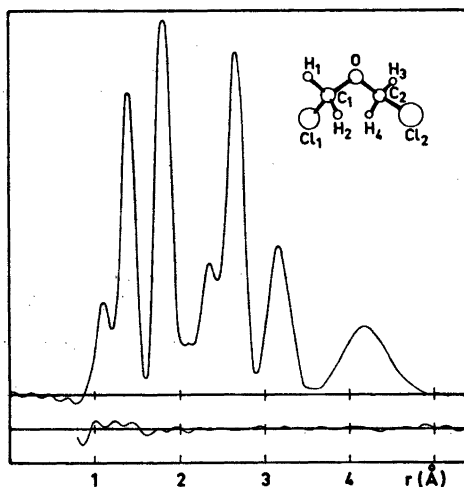


Fig. 3. Bis(chloromethyl) ether. Experimental radial distribution curve. The lower curve shows the difference between the experimental and the theoretical values. Artificial damping constant $k=0.0015$ Å.

spond to the C-H, C-O, and C-Cl bond distances, respectively. The next two peaks at 2.3 and 2.7 Å represent mainly distances over one angle, the most important contributions being C(1)···C(2), Cl(1)···H(1), and Cl···O. Also the three shortest Cl···H distances between different chloromethyl groups contribute to these peaks.

The two outer peaks in the RD curve at about 3.2 and 4.2 Å contain information about the conformation of the molecule. The C···Cl and Cl···Cl distances come in this region.

If the peak at 3.2 Å represented the Cl···Cl distance, this would be considerably shorter than the sum of the van der Waals' radii. It is therefore reasonable to assume that the Cl···Cl distance corresponds to the 4.2 Å peak. If this is so, the peak at 3.2 Å represents one or both of the non-bonded C···Cl distances. The remaining distances in the outer part of the RD-curve are Cl···H and H···H distances. However, their contribution is too small to give any indication of which conformers could be present. The theoretical models used in these investigations are all based on the assumption that the valence angles and bond distances are equal in both of the -O-CH₂Cl groups of the molecule.

Fig. 4 shows the outer part of the experimental RD-curve compared with the corre-

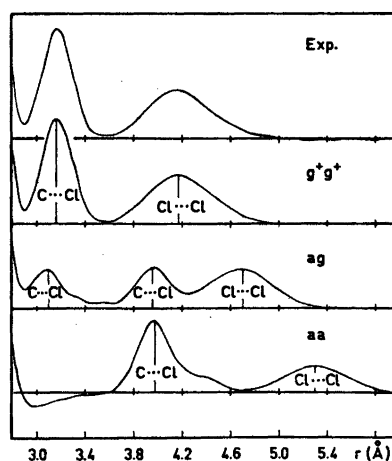


Fig. 4. Bis(chloromethyl) ether. The outer part of the experimental radial distribution curve compared with the corresponding part of the theoretical radial distribution curves for the three conformations: $g^{\pm}g^{\pm}$, ag , and aa .

Table 1. Structure parameters for bis(chloromethyl) ether. Distances (r_a -values) and mean amplitudes of vibration (u -values) are given in Å, angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation. The uncertainty arising from error in the electron wavelength is included. (For numbering system of the atoms see Fig. 3.)

Distances	r	u
C-O	1.393(3)	0.043(6)
C-H	1.100(12)	0.070
Cl-C	1.800(3)	0.052(5)
Cl ₁ ...Cl ₂	4.232(36)	0.269(32)
Cl...O	2.660(6)	0.064(6)
Cl...C	3.150(10)	0.111(9)
C ₁ ...C ₂	2.340(21)	0.084(33)
Cl ₁ ...H ₁	2.367(19)	0.078
Cl ₁ ...H ₄	2.700(32)	0.135
Cl ₁ ...H ₃	4.035(26)	0.149
O...H	2.069(37)	0.097
C ₁ ...H ₄	2.573(28)	0.077
C ₁ ...H ₃	3.293(43)	0.101

Angles	
∠COC	114.2(1.5)
∠OCCl	112.2(0.8)
∠OCH	111.6(2.2)
δ(ClCOC) ^a	69.6(1.6)

^a δ is the dihedral angle ClCOC.

responding part of the theoretical RD-curves for the three conformers: the g^+g^+ (dihedral angle Cl-C-O-C, $\delta=69.60$), ag ($\delta=60.0$ and 180.0°) and aa . The *anti-anti* conformation is seen to result in a Cl...Cl distance outside the range of the experimental distances. Also the Cl...C distances at about 3.9 Å are too long to fit the peak at 3.2 Å, although the shapes of these peaks are comparable. This conformer does not seem to be present.

Also in the *anti-gauche* conformation the Cl...Cl distance is seen to be too long. The Cl...C distances in this conformation are separated into two peaks, due to the unequal dihedral angles Cl-C-O-C. A comparison of the area underneath these peaks with the experimental RD-curve suggests that the Cl...C distances should be of almost equal lengths in order to fit the experimental curve. The third possibility - the staggered conformation g^+g^+ - shows a good fit to the experimental curves. A least-squares refinement of the twist angles about the C-O bonds results in a Cl-C-O-C dihedral angle of 69.6° . The two Cl...C distances are then 3.150 Å and the corresponding vibrational amplitudes 0.111 Å. A refinement of the two twist angles independently is, for convergency reasons, only

Table 2. Correlation matrix ($\times 100$) for the parameters. (The coefficients having absolute values less than 30 are not given.)

Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 r(C-O)	100														
2 ∠COC		100													
3 r(C-H)			100												
4 r(Cl-C)				100											
5 ∠OCH			62	-32	43	100									
6 ∠OCCl		-37	-48	31	-61	-78	100								
7 δ(ClCOC)			88		45		100								
8 u(C-O)			-39		47	-35		100							
9 u(Cl-C)					53	-43		65	100						
10 u(Cl...Cl)					35				32	100					
11 u(Cl...O)		48			59	-45	41	50	58	31	100				
12 u(Cl...C)											100				
13 u(C...C)			-32		44	-32		30				100			
14 u(O...H)					-36	32		-39	-32				-40	100	
15 scale			-40		63	-48		75	77	39	67		37	46	100

possible when the u -values for the Cl \cdots C distances are kept at fixed values. From the experimental curves there is no evidence of any admixture of other conformers of bis(chloromethyl) ether in the gas phase.

It was necessary during the least-squares refinement to keep the u -values for non-bonded Cl \cdots H, C \cdots H, and H \cdots H at fixed values in order to obtain convergency.

The final structural parameters are found in Table 1. The correlation matrix is given in Table 2.

As was expected, the molecule possesses a C_2 symmetry and a *gauche-gauche* conformation. An all-*anti* conformation would result in unfavourable interactions between non-bonded electrons on the oxygen and the halogen atoms. For comparison it may be mentioned that also 1,3-dibromopropane,⁹ where the ether oxygen is replaced by an electrophile CH₂ group, contains 67 % of the *gauche-gauche* conformation, 3 % of the all-*anti* conformation, and 30 % of the *anti-gauche* conformation. In that compound a certain contribution of the *anti* conformer may be explained by a possible stabilization due to a bromine-hydrogen interaction. Such a stabilization is not present in bis(chloromethyl) ether.

The C—O bond distances in this molecule ($1.393 \pm 0.003 \text{ \AA}$) are somewhat smaller than usually found in aliphatic ethers.¹⁰ Comparison with the gas phase structure of ClCH₂—O—CH₂ determined by electron diffraction by Planje *et al.*¹¹ shows, however, an even shorter C—O bond length (1.368 Å) for the chloromethoxy group. As pointed out in their article, two different C—O bond distances are presented in the same unresolved peak in their RD-curve. By fixing the vibrational amplitudes to what they assume a reasonable value for C—O bond distances, they determined the two C—O bond lengths to be 1.368 and 1.414 Å. However, a large uncertainty is connected with this procedure and standard deviations for these distances are not given.

The structure of chloromethyl methyl ether has also been investigated by Akishin *et al.*¹² with the electron diffraction method. It seems from their article that only an average C—O bond distance ($1.42 \pm 0.03 \text{ \AA}$) is determined.

The Cl—C bond lengths in this work ($1.800 \pm 0.003 \text{ \AA}$) are in good agreement with that

found by Planje *et al.*¹¹ (1.813 Å), but appreciably smaller than the 1.87 Å, determined by Akishin *et al.*¹² It is seen that the C—O and C—Cl bond lengths in ClCH₂—O—CH₂Cl are somewhat shorter and longer, respectively, than the corresponding distances in chloroalkanes and aliphatic ethers. This observation is by no means new, and it has been explained by Lucken¹³ in 1959 and further supported by Williams in 1961¹⁴ and 1962¹⁵ as a partial double-bond due to charge migration from the reactive lone pair electron orbital to the anti-bonding σ -orbital of the C—Cl bonds. Williams concludes that such double-bonding in saturated aliphatic compounds is enhanced by increase in electronegativity of the acceptor atom and becomes more pronounced as the reactivity of the lone pair increases (N > O > F > Cl, Br > I).

The dihedral angle Cl—C—O—C of $69.6 \pm 1.6^\circ$ found in this investigation of bis(chloromethyl) ether is in reasonably good agreement with the corresponding dihedral angles in chloromethyl methyl ether determined by Planje *et al.* and Akishin *et al.* to 74.3 and $76 \pm 5^\circ$, respectively.

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