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The Molecular Structure and Conformation of Dichloromethyl Methyl Ether, $Cl_2HC—O—CH_3$, in the Gas Phase

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The molecular structure and conformation of dichloromethyl methyl ether have been investigated in the gas phase by the electron-diffraction method. As expected, a shortening of the C–O bond compared to the corresponding bond in unsubstituted ethers and a lengthening of the C–Cl bond compared to chlorine-substituted alkanes are observed for this compound. From the analysis of dichloromethyl methyl ether the conclusion may be drawn that the *gauche-gauche* conformation, where the two dihedral angles δ(ClCOC) are (+)*gauche* and (−)-*gauche*, ($\pm 60.6°$), is strongly preferred.

The following parameters have been determined: $r(C-O)_{CH_3} = 1.405(9)$ Å, $r(C-O)_{CHCl_2} = 1.383(9)$ Å, $r(C-H) = 1.161(12)$ Å, $r(C-Cl) = 1.798(3)$ Å, $\angle COC = 118.6(2.1)°$, $\angle OCCl = 111.8(1.5)°$, $\angle OCH_{CH_3} = 112.5°$, $\delta ClC(2)OC(1) = 60.6(1.6)°$, $\delta H(1)C(1)OC(2) = 30.3(6.3)°$.

The molecular conformation of chloromethyl methyl ether and bis(chloromethyl) ether have already been investigated by different methods, *i.e.* dipole moments,[1–3] Raman,[4] infrared,[5–7] and microwave spectroscopy[8] and electron diffraction.[9,10] The conclusion obtained by all but one[6] of these investigations is that there is a preference for the chlorine atoms to be in *gauche* relation to the COC chain. Charles *et al.*[7] also report small amounts of molecules with *anti* dihedral angles δClCOC to be present for bis(chloromethyl) ether, while Chiba[1] suggests from his data the existence of slightly different conformers among which the *gauche* conformation has the lowest energy.

It was therefore of interest to investigate the molecular structure and conformation of dichloromethyl methyl ether (Fig. 1) in the gas phase by the electron diffraction method in order to see whether the chlorine atoms both prefer the *gauche* position (g^+g^-) or if the *anti* conformer (*ag*) is also present.

EXPERIMENTAL

The sample of dichloromethyl methyl ether used in this investigation was obtained from Fluka and was purified by GLC. The electron diffraction diagrams were taken on a Balzers Eldigraph KD G2. The pressure in the apparatus during the exposure was approximately 5×10^{-5} Torr. The sample temperature was kept at about 23 °C. The diffraction diagrams were recorded at two different nozzle-to-plate distances, *i.e.* 25.00 and 50.00 cm. The accelerating voltage of the electrons was approximately 42 kV, corresponding to a wavelength of the electrons of 0.05845 and 0.05848 Å, respectively. Four selected plates from each nozzle-to-plate distance were used in the analysis. The intensities were modified by $s/|f_C'||f_O'|$, where $|f'|$ is the scattering amplitude[11,12] for carbon and oxygen.

The experimental data were analysed in the usual way.[13] The experimental data obtained cover scattering angles corresponding to an s-range of 1.5–29.75 $Å^{-1}$. The molecular intensity curve is shown in Fig. 2.

The calculations have been carried out on CDC 3300 and CDC 7400(CYBER) computers.[13]

STRUCTURE ANALYSIS

Approximate values for the molecular parameters were estimated from the experimental radial distribution (RD) curve (Fig. 3) and refined by the least-squares procedure.

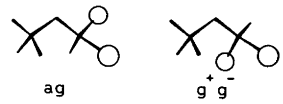

Fig. 1. Dichloromethyl methyl ether. The two distinguishable staggered conformations: *anti-gauche* (*ag*) and *gauche*(+)-*gauche*(−) (g^+g^-).

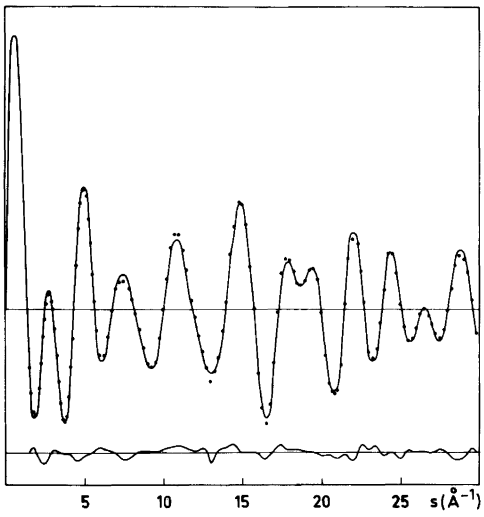

Fig. 2. Dichloromethyl methyl ether. Theoretical molecular intensity curve. The dots show the experimental values. The lower curve shows the difference between the experimental and the theoretical values.

The first peak at about 1.4 Å in the RD curve shows a shoulder at 1.16 Å, corresponding to the four C–H bond distances. Any possible difference in the C–H bond length in the methyl and dichloromethyl groups cannot be determined by this method. All the C–H distances are therefore assumed to be equal. The main peak at 1.4 Å contains the two C–O bond distances. As it has earlier been found that chlorine substitution on carbon atoms in α-position to an ether oxygen atom results in a decrease of the C–O bond length,[9,10] the two C–O bonds in dichloromethyl methyl ether were expected to be of different lengths. Due to the large correlation between the two C–O bonds and the corresponding vibrational amplitudes, the refinement of the parameters is only possible when some of the parameters are kept at fixed values during the refinement. It then seems fairly reasonable to assume the vibrational amplitudes (u-values) for the two C–O distances to be equal and of the same magnitude as the corresponding u-values in $ClCH_2-O-CH_2Cl$,[10] where the two C–O bonds are equal and therefore determined with larger accuracy. In the further refinement of the parameters these u-values were kept at fixed values (0.043 Å). The refinement of the carbon oxygen bond distances then results in a shorter length of 1.383 Å for the dichloromethoxy group and a length of 1.410 Å for the methoxy group. The well-resolved peak at 1.8 Å corresponds to the two Cl–C bond distances.

The C···C and Cl···H distances over one angle are found in the small peak at 2.4 Å, while the peak at 2.6 Å is mainly due to the two Cl···O distances. The Cl···Cl distance appears with large weight in the RD curve at 2.9 Å.

The conformation of the Cl–C–O–C skeleton may be determined from the non-bonded C···Cl distances [C(1)···Cl(1) and C(1)···Cl(2)]. As there are no pronounced peaks in the RD curve outside the shoulder at about 3.1 Å, the two C···Cl distances must come in this region. From Fig. 3 this is seen to give a good agreement between experimental and

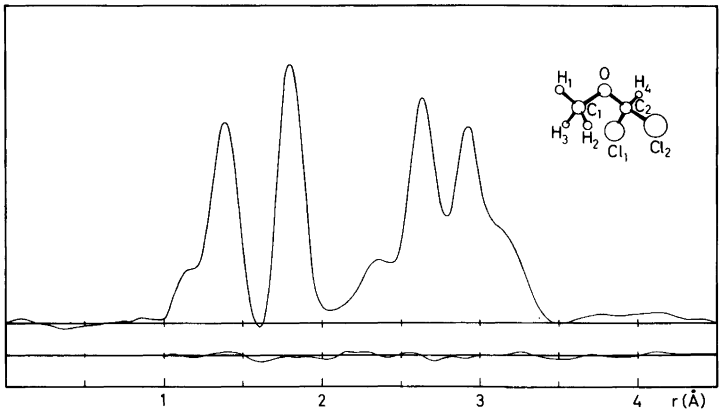

Fig. 3. Dichloromethyl methyl ether. Experimental radial distribution curve. The lower curve shows the difference between the experimental and the theoretical values. Artifical damping constant $k=0.0020$ Å.

theoretical data. Within the standard deviation the two Cl−C−O−C dihedral angles are found to be equal. In the final refinement the two dihedral angles ClC(2)OC(1) and Cl(2)C(2)OC(1) have therefore been assumed to be of the same magnitude with one chlorine atom on each side of the molecular plane.

By twisting the $CHCl_2$ group from a g^+g^- to an *ag* conformation one C···Cl distance is shifted from about 3.1 Å to about 4.0 Å. Refinements including both a g^+g^- and an *ag* conformation in mixture result in a contribution of approximately 4 % of the *ag* conformer. As, however, the standard deviation is larger than the determined percentage, the presence of the *ag* conformer is doubtful.

The poor scattering of electrons by hydrogen atoms makes the determination of hydrogen atom positions difficult by electron diffraction. As a consequence of this, it is not possible to obtain convergency in the least-squares refinement of the OCH angle. This angle, therefore, has been determined by trial and error.

When the three O···H distances from oxygen to methyl hydrogen atoms are of equal lengths, this will result in a disagreement between the experimental and theoretical RD curves at about 2.1 Å. An apparently better correspondance in this region is obtained by tilting the methyl group in such a way that the three-fold axis of the methyl group makes an angle with the $O-CH_3$ axis. However, as the error of square residuals is not decreased by introduction of the tilt parameter, and as the standard deviation of the tilt angle is very large, the tilt is not included.

The only information of any significance about the methyl hydrogen atom positions is given by the non-bonded Cl···H distances, and, unfortunately, even these distances appear with fairly small weight

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

No.	Parameter	r_a	*u*
1	C(1)−O	1.405(9)	0.043[a]
2	C(2)−O	1.383(9)	
3	C−H	1.161(12)	0.078
4	C−Cl	1.798(3)	0.042
5	Cl···Cl	2.909(5)	0.064(7)
6	Cl···O	2.644(3)	0.051(6)
7	Cl···C	3.114(12)	0.105(16)
8	C···C	2.397(14)	0.085(30)
9	Cl···H(4)	2.378(17)	0.085
10	Cl(2)···H(3)	3.970(85)	
11	Cl(2)···H(2)	2.661(66)	
12	Cl(2)···H(1)	3.887(71)	0.16−0.20
13	Cl(1)···H(3)	3.096(89)	
14	Cl(1)···H(2)	3.183(99)	
15	Cl(1)···H(1)	4.268(37)	
16	O···H(1)	2.068(60)	0.14
17	O···H(4)	2.149(71)	
18	∠COC	118.6(2.1)	
19	∠OCH(1)	112.5	
20	∠OCCl	111.8(1.5)	
21	∠OCH(4)	115.0	
22	∠ClCCl	108.0	
23	δClC(2)O	60.6(1.6)	
24	δH(4)C(2)OC(1)	180.0	
25	δH(2)C(1)OC(2)	30.3(6.3)	

[a] Fixed during refinement.

Table 2. Elements of the correlation matrix (× 100). Only elements [ρ(i,j)] of absolute values larger than 0.5 are given. The number associated with the distances, *r*; angles, ∠; and *u*-values, *u*, refer to those given in the parameter list, Table 1.

ρ(r1/r2)	−85	ρ(r1/∠18)	−64	ρ(r1/∠20)	78	ρ(r1/∠23)	64
ρ(r2/∠18)	63	ρ(r2/∠20)	−92	ρ(r2/∠23)	−76	ρ(r2/u6)	68
ρ(r3/u6)	−65	ρ(r3/u7)	82				
ρ(∠18/∠20)	−72	ρ(∠18/∠23)	−69	ρ(∠18/∠25)	85		
ρ(∠20/∠23)	91						
ρ(∠23/∠25)	63						
ρ(u7/u5)	82						

in the curves. The best agreement between experimental and theoretical curves is obtained for a dihedral angle δ H(2)C(1)OC(2) of 30.3° (6.3°).

As the peak at about 3.7−4.4 Å, containing mainly Cl···H distances, is not very pronounced, and as the Cl···H lengths are not very sensitive to small changes in the twist angle, the standard deviation for this angle is seen to be large.

In order to obtain convergency in the least-squares refinement it was necessary to keep not only the OCH angle and the *u*(C−O) at fixed values during the refinement, but also the *u*-values for non-bonded Cl···H, O···H, C···H and H···H distances. Keeping some parameters at fixed values during the refinement results in too small standard deviations for some of the parameters. To compensate for this the approach proposed by Seip[14] has been applied to some of the more important parameters. The final parameters are shown in Table 1 and elements from the correlation matrix in Table 2.

DISCUSSION

From the electron diffraction investigation of $Cl_2HC-O-CH_3$ it may be concluded that the only conformer present in the gas phase is the (+)*gauche*-(−)*gauche* conformer, where both chlorine atoms are in *gauche* positions relative to the COC chain on each side of the molecular plane. This result further supports the preference for a *gauche* conformation for the ClCOC skeleton, which has also been found for $ClH_2C-O-CH_3$[9] and $ClH_2C-O-CH_2Cl$.[10]

For comparison and in contrast to this it can be mentioned that halosubstituted alkanes usually exist as conformational mixtures.[15,16] This strong preference for *gauche* conformations when CH_2 groups in alkanes are replaced by the isoelectronic ether oxygen atom most probably is related to the oxygen lone pair electrons. A qualitative model may explain this: a repulsive interaction between lone pair electrons on oxygen and on α-substituted halogen will favour a conformation where the negative charges are further apart. The preferred conformation for the chlorine atom in α-halogeno-ethers will therefore be the *gauche* conformation, when other effects influencing the conformation are negligible. However, by exchange of the electronegative oxygen atom by a CH_2 group such repulsive interactions will not be present and therefore *anti* conformation for the halogen−C−CH_2−C dihedral angles may be present.

The two C−O bond distances in dichloromethyl methyl ether have been found to be of different lengths, *i.e.* 1.383 and 1.405 Å. In agreement with the C−O bond lengths determined for $ClH_2C-O-CH_2Cl$[10] (1.393 Å) and $ClH_2C-O-CH_3$[9] (1.368 and 1.410 Å), a shortening of the C−O bond in the chloro-methoxy group as compared to unsubstituted ethers has been observed. Simultaneously, a lengthening of the C−Cl distance [1.798(3) Å] as compared to chloro-alkanes [Ref. 20: 1.774(4) Å] has been found. These changes in the bond lengths due to chlorine substitution in ethers were first explained by Lucken[17] in 1959 and further supported by Williams in 1961[18] and 1962,[19] as a partial double bond due to charge migration from the reactive oxygen lone pair electron orbital to the antibonding σ*-orbital of the C−Cl bond. Consequently the shortening of the C−O bond must be accompanied by a lengthening of the C−Cl bond.

However, large uncertainties in the values of the C−O bonds are found for both $Cl_2HC-O-CH_3$ and $ClH_2C-O-CH_3$, because the two different C−O distances are present in the same unresolved peak in the RD curve and are strongly correlated (Table 2).

The dihedral angle Cl−C−O−C of 60.6° (1.6°) found in this investigation of dichloromethyl methyl ether is somewhat smaller than the corresponding dihedral angles found for bis(chloromethyl) ether[10] and chloromethyl methyl ether[9] (69.6 and 74.3°, respectively). However, the angle Cl−C−Cl in this molecule (108.0°) is in good agreement with the Cl−C−Cl angles determined for 1,1-dichloro-substituted propanes.[20,21]

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REFERENCES

1. Chiba, T. *Bull. Chem. Soc. Jpn 28* (1955) 295.
2. Morino, Y., Shiio, H. and Miyagawa, I. *Rep. Radiat. Chem. Res. Inst. Tokyo Univ. 5* (1950) 6.
3. Borovikov, Yu. Ya., Topchii, V. A., Mester, B. S. and Tarasenko, V. S. *Zh. Org. Khim. 12* (1976) 280 (Eng.).
4. Katayama, M. and Morino, Y. *Rep. Radiat. Chem. Res. Inst. Tokyo Univ. 4* (1949) 1.
5. Mizushima, S., Shimanouchi, T., Miyazawa, T. and Hayashi, M. *Unpublished.*
6. Jones, R. G. and Orville-Thomas, W. J. *J. Chem. Soc.* (1964) 692.
7. Charles, S. W., Cullen, F. C. and Owen, N. L. *Spectrochim. Acta A 32* (1976) 1171.
8. Ikeda, T., Curl, Jr., F. R. and Karlsson, H. *J. Mol. Spectrosc. 53* (1974) 101.
9. Planje, M. C., Toneman, L. H. and Dallinga, G. *Recl. Trav. Chim. Pays-Bas 84* (1965) 232.
10. Astrup, E. E. and Aomar, A. M. *Acta Chem. Scand. A 30* (1976) 289.
11. Peacher, J. and Wills, J. C. *J. Chem. Phys. 46* (1967) 4809.
12. Strand, T. G. and Bonham, R. A. *J. Chem. Phys. 40* (1964) 1686.
13. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
14. Seip, H. M. *A Specialist Periodical Report: Molecular Structure by Diffraction Methods*, The Chemical Society, London 1973, Vol. 1, p. 53.
15. Farup, P. E. and Stølevik, R. *Acta Chem. Scand. A 28* (1974) 680.
16. Morino, Y. and Kuchitsu, K. *J. Chem. Phys. 28* (1958) 175.
17. Lucken, E. A. C. *J. Chem. Soc.* (1959) 2954.
18. Williams, J. F. A. *Trans. Faraday Soc. 57* (1961) 2989.
19. Williams, J. F. A. *Tetrahedron 18* (1962) 1477.
20. Johnsen, J. P. and Stølevik, R. *Acta Chem. Scand. A 29* (1975) 457.
21. Fernholt, L. and Stølevik, R. *Acta Chem. Scand. A 29* (1975) 651.

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