

An Investigation of the Molecular Structure and Conformation of 1,2-Dimethoxyethane, $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$, in the Gas Phase

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1,2-Dimethoxyethane has been investigated in the gas phase by the electron diffraction method. Satisfactory agreement between experimental and theoretical data cannot be obtained for any single conformer. However, several mixtures of two conformers give acceptable correspondence to the experimental data. From electron diffraction data it is therefore impossible to obtain one unique solution to the problem. The best fit is obtained for a mixture composed mainly of *aaa*, *aga*, and *agg* conformers, but minor contributions of *aag*, *gag* and *ggg* cannot be excluded. The following molecular parameters have been determined: $r(\text{O}-\text{C}) = 1.410(3) \text{ \AA}$, $r(\text{C}-\text{C}) = 1.504 \text{ \AA}$ (assumed), $r(\text{C}-\text{H}) = 1.109(4) \text{ \AA}$, $\text{COC} = 110.7(1.4)^\circ$, $\text{OCC} = 113.2(1.6)^\circ$, $\text{CCH} = 110.0^\circ$, $\text{OCH} = 110.1^\circ$, $(\text{OCCO})_{\text{gauche}} = 61.9(7.8)^\circ$, $(\text{OCCO})_{\text{anti}} = -172.2(22.0)^\circ$, $(\text{COCC})_{\text{gauche}} = 88.7(3.3)^\circ$, $(\text{COCC})_{\text{anti}} = 152.4(6.0)^\circ$.

As part of a study of molecular structures and conformations of cyclic¹ and acyclic ethers²⁻⁶ it was of interest to investigate the conformation in the gas phase of the unit $\text{C}-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}$, where the oxygen atoms in the chain are separated by two carbon atoms. Earlier investigations of the chain $\text{C}-\text{O}-\text{C}-\text{O}-\text{C}$ ^{2,3} show a strong preference for the *gauche*(±)*gauche*(±) conformation, probably caused by a $1,4\text{-CH}\cdots\text{O}$ attraction.⁷ As such interaction is not possible in 1,2-dimethoxyethane, where both 1 and 4 positions are occupied by oxygen atoms or by carbon atoms, it was the aim of this investigation to find out whether this molecule has any preferred conformer or exists as a mixture of several conformers in the gas phase.

The ethyleneglycol dimethyl ethers ($\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$) are known to have

a good solvent effect on proton donors.⁸⁻¹¹ Although the most effective complexing agents are those containing several oxygen atoms, also dimethoxyethane ($n=1$) may form relatively stable complexes with, *e.g.*, alkali and alkaline earth metal ions⁸ or proton donors like organolithium compounds.¹¹ An *OCCO gauche* conformation in these chains should be favourable for the formation of complexes where two or more oxygen atoms from the same ether molecule participate in the solvation of a metal ion.

1,2-Dimethoxyethane has previously been investigated in the liquid and the solid state and in solution by infrared, Raman and NMR spectroscopic methods^{12,14-19,22} and by dipole moment measurements.^{20,21} Also a theoretical analysis of the conformational equilibrium mixture, based on classical semi-empirical potential functions, has been carried out for 1,2-dimethoxyethane.¹³ While the *anti-gauche-anti* conformation is the only conformer in the crystalline state, most of the investigations in the liquid state concluded with an equilibrium mixture of several conformers where a *gauche* dihedral angle $\text{OC}-\text{CO}$ is slightly preferred to an *anti*. The infrared spectroscopic investigation by Iwamoto,¹⁵ however, considers an *anti* dihedral angle $\text{OC}-\text{CO}$ to be the most stable in the liquid state. He further concludes with the following sequence of conformations with decreasing stability: *aaa*, *aga*, *gaa*, *agg* for 1,2-dimethoxyethane in the pure liquid, while other groups²² conclude that four conformers are present in the gas and liquid phase without indicating which these conformers are. The preference for an *anti* $\text{OC}-\text{CO}$ dihedral angle is supported by Podo

*et al.*¹³ in their theoretical calculations for the gaseous state of 1,2-dimethoxyethane, but also this group finds the *gauche* OC–CO angle to be the more stable in the liquid. From that investigation the difference between an *anti* and a *gauche* OC–CO dihedral angle is estimated to be about 0.4 kJ/mol, while the energy difference between *anti* and *gauche* of the CC–OC dihedral angle is about 4.5 kJ/mol. An additional energy increase of 1.3–2.0 kJ/mol is calculated for the g^+g^- sequence of the dihedral angles in the chain.

EXPERIMENTAL

The sample of 1,2-dimethoxyethane used in this investigation was obtained from Koch-Light Laboratories.

The electron diffraction diagrams were taken on a Balzers Eldigraph KDG2. The sample temperature was kept at about 0 °C during the exposures, and the pressure in the apparatus was approximately 1×10^{-5} Torr. The diffraction diagrams were recorded at 482.00 and 232.00 mm nozzle-to-plate distances, the electron wavelengths being 0.05843 and 0.05847 Å, respectively. Four selected plates were analysed for each nozzle-to-plate distance. The intensity was recorded on a photometer for each 0.25 mm on the photographic plates. Each plate was oscillated about the center of the diffraction diagrams, and the intensity integrated over the arc. The data were treated the usual way.²³

An empirical background was subtracted from the data for each plate before averaging the intensity data. The intensities were modified by $s/|f'_o| \cdot |f'_c|$, where $|f'|$ is the scattering amplitudes^{24,25} for

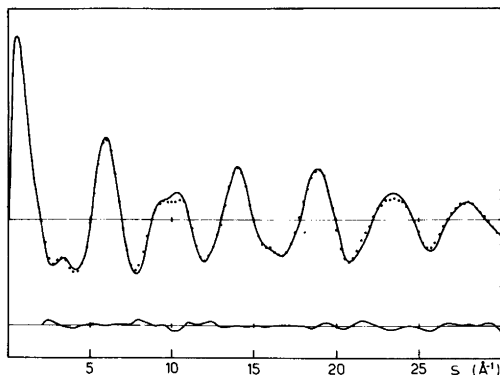


Fig. 1. 1,2-Dimethoxyethane. Theoretical molecular intensity curve for an equilibrium mixture of six rotamers. The dots show the experimental values. The lower curve shows the difference between the experimental and theoretical values.

oxygen and carbon. The experimental data obtained cover scattering angles corresponding to an s -range of $1.75-30.00 \text{ \AA}^{-1}$.

The molecular intensity curve is shown in Fig. 1. A least-squares procedure was used to refine the distances and vibrational amplitudes estimated from the experimental radial distribution (RD) curve. The RD curve has been obtained by Fourier transformation of the molecular intensity curve.

The calculations have been carried out on CDC 3300 and CDC 7400 (CYBER) computers.²³

STRUCTURAL ANALYSIS AND DISCUSSION

Approximate values for the structure parameters used in the least-squares analysis are determined from the experimental RD curve shown in Fig. 2A.

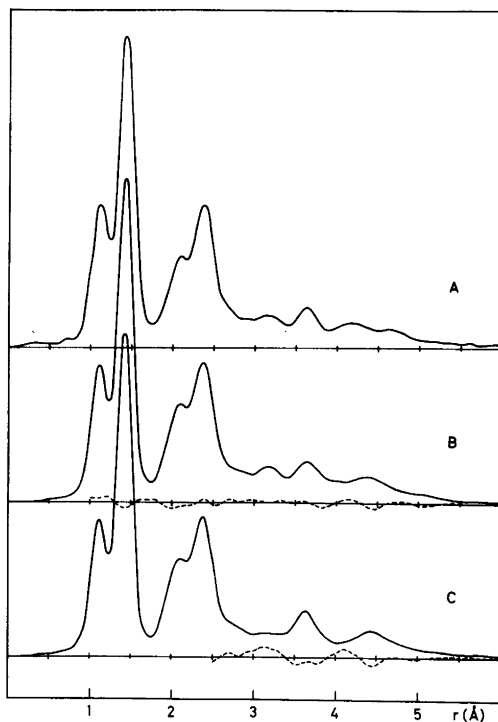


Fig. 2. 1,2-Dimethoxyethane. A: Experimental radial distribution curve. B: Theoretical RD curve containing all the six distinguishable conformers, the percentage contributions of which are listed in Table 4. C: Theoretical RD curve corresponding to the population of conformers calculated by Podo *et al.* The broken lines in curve B and C show the difference between experimental and theoretical curves. Artificial damping constant $k = 0.0022 \text{ \AA}$.

Table 1. Structure parameters for 1,2-dimethoxyethane. The bond distances and valence angles are obtained by least-squares refinement on the intensity data of single conformations. The dihedral angles $\delta(\text{OCCO})$ *gauche*, $\delta(\text{OCCO})$ *anti*, $\delta(\text{COCC})$ *gauche* and $\delta(\text{COCC})$ *anti* are determined from the equilibrium mixture of six conformers. Distances (r_s -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 of the atoms see Fig. 3).

Conformation	B <i>ggg</i>	C <i>aaa</i>	D <i>aga</i>	E <i>gag</i>	F <i>gaa</i>	G <i>agg</i>
Distances						
O—C	1.410	1.410(3)	1.410(3)	1.410	1.410	1.410
C—C	1.504 ^a	1.504 ^a	1.504 ^a	1.504 ^a	1.504 ^a	1.504 ^a
C—H	1.109	1.109(4)	1.109(4)	1.109	1.109	1.109
O(1)···C(3)	2.447	2.447(8)	2.447(8)	2.447	2.447	2.447
C(3)···C(4)	2.319	2.319(9)	2.319(9)	2.319	2.319	2.319
O(1)···O(2)	2.950	3.689(21)	2.950(28)	3.689	3.689	2.950
C(2)···C(4)	} 3.146	} 3.639(19)	} 3.639(18)	} 3.146	3.146	3.639
C(1)···C(3)					3.639	3.146
O(1)···C(4)	} 3.904	} 4.696(45)	} 4.333(46)	} 4.295	4.295	4.333
O(2)···C(1)					4.696	3.904
C(1)···C(4)	5.044	5.743(59)	5.693(40)	4.471	5.064	5.196
Angles						
$\angle \text{COC}$	110.7	110.7(1.4)	110.7(1.4)	110.7	110.7	110.7
$\angle \text{OCC}$	113.2	113.2(1.6)	113.2(1.6)	113.2	113.2	113.2
$\angle \text{CCH}$	110.0	110.0	110.0	110.0	110.0	110.0
$\angle \text{OCH}$	110.1	110.1	110.1	110.1	110.1	110.1
$\delta(\text{OCCO}), \alpha$	61.9 (7.8)	-172.2(22.0)	61.9(7.8)	-172.2	-172.2	61.9
$\delta(\text{COCC}) \left\{ \begin{array}{l} \beta \\ \gamma \end{array} \right.$	} 88.7(3.3)	} 152.4(6.0)	} 152.4(6.0)	} 88.7	88.7	152.4
					152.4	88.7

^a Fixed value, Ref. 26, 27.

The first two peaks in the RD curve represent the bond distances in the molecule. The peak at 1.1 Å corresponds to the ten C—H distances, while the C—C and the four O—C distances are found in the peak at about 1.4 Å. In the structure of dimethoxymethane² a difference of 0.05 Å has been observed between terminal and central O—C bonds. A similar difference between the O—C bonds in dimethoxyethane cannot be determined from the electron diffraction data, and therefore the average value, 1.410 Å, is reported here. Nor can the C—C bond distance be determined with great accuracy due to the correlation with the O—C bond ($\rho=0.68$) and to the small weight of this distance compared to the four O—C bond distances. Any length between 1.49–1.52 Å gives a

satisfactory agreement with the experimental data. The C—C distance has therefore been fixed at 1.504 Å, which is the average value of C—C bonds in —O—C—C—O— units in some X-ray investigations of larger ring systems.^{26,27}

The small peak at 2.1 Å shows the shortest non-bonded O···H and C···H distances. The next peak at 2.4 Å represents mainly C···C and O···C distances over one valence angle. The C(3)O(2)C(4) and the C(1)O(1)C(2) angles are assumed to be equal. Also the two OCC angles are assumed equal.

Because of the poor scattering of electrons by hydrogen atoms, the positions of these atoms could not be accurately determined from the electron diffraction data. During the conformational analysis the methyl groups, assumed to have a three-fold

symmetry, have therefore been kept in fixed positions, staggered to the O–C bonds. Further, the methylene groups are assumed to have a local C_{2v} symmetry.

The part of the RD curve, which contains information about the conformation of the molecule is found outside 2.7 Å. As may be seen from Fig. 2A, this part of the curve mostly does not contain well-resolved peaks. The most pronounced maximum in this region is found at 3.6 Å, while there are also indications of maxima around 3.1, 4.2 and 4.7 Å. Such a fairly smooth RD curve would be expected if many different interatomic distances are present and therefore suggests the presence of several conformers, in agreement with the spectroscopic investigations. However, even in a mixture of several conformers particular dihedral angles may still be preferred.

The main contribution to the conformation-dependent part of the RD curve stems from the $O\cdots O$, $C(1)\cdots C(3)$, $C(2)\cdots C(4)$, $O(2)\cdots C(1)$, $O(1)\cdots C(4)$ and $C(1)\cdots C(4)$ distances. The lengths of three of these distances, i.e. $O\cdots O$, $C(1)\cdots C(3)$, and $C(2)\cdots C(4)$, depend on only one dihedral angle, α , β and γ , respectively (Fig. 3), while the lengths of the two $O\cdots C$ distances depend on two dihedral angles, α and β or γ . The long $C(1)\cdots C(4)$ distance is dependent on

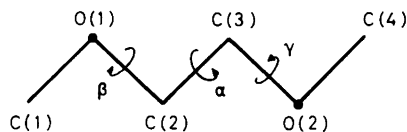


Fig. 3. 1,2-Dimethoxyethane. Model showing the numbering of the atoms and the dihedral angles α , β , and γ .

all the three dihedral angles, but as the weight of a distance in the RD curve is inversely proportional to the interatomic length, the contribution from a long distance to the RD curve may be negligible.

Gauche dihedral angles (β , γ about 90° , α about 60°) give rise to 1,4-distances ($C\cdots C$ and $O\cdots C$) of about 3.1 Å, while *anti* dihedral angles (β , γ about 150° , α about 180°) result in displacement of these distances to about 3.6 Å. Fig. 4, is a graphical representation showing the relation between the $CC-OC$ and $OC-CO$ dihedral angles and the 1,4- $C\cdots C$ and $O\cdots O$ distances for the various conformers. The individual conformers where $\beta = \gamma$ are represented by the rings, while those having $\beta \neq \gamma$ are shown as arrows indicating a mixture of two rings, giving two different $C\cdots C$ distances.

Due to the presence of dihedral angles g^+ and g^-

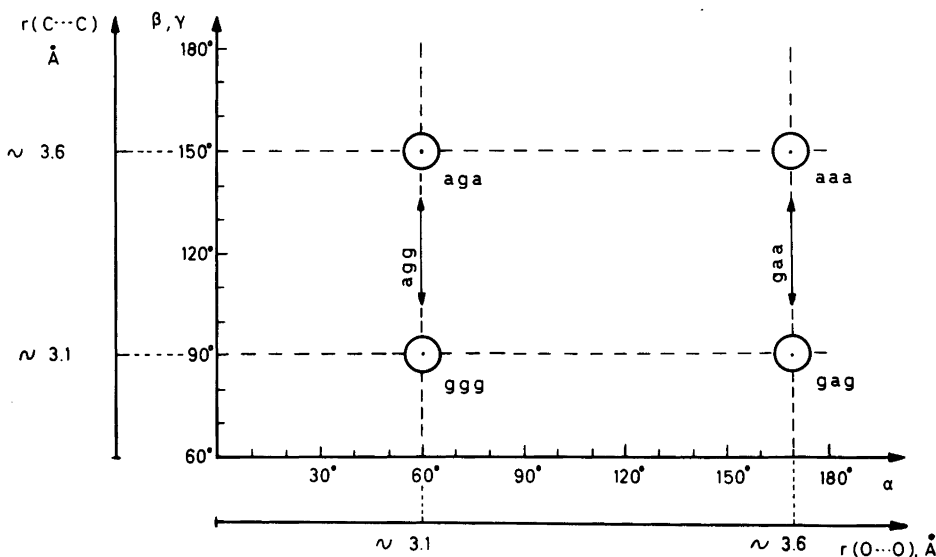


Fig. 4. 1,2-Dimethoxyethane. A graphical representation of the rotation angles $OCCO$ (α) and $COCC$ (β and γ). The four rotamers, for which $\beta = \gamma$, their dihedral angles, and corresponding interatomic distances, are represented by the circles. The two rotamers, for which $\beta \neq \gamma$, are represented by a mixture of two circles, as indicated by the arrows.

Table 2. Vibrational amplitudes (u -values) for 1,2-dimethoxyethane. The u -values are given in Å. For the shorter distances the values have been determined by refinements in separate cycles of a small number of parameters. For the longer distances the values have been determined by a normal coordinate analysis.

Distances	u
O—C	0.052(4)
C—C	0.054(12)
C—H	0.061(6)
O(1)···C(3)	0.062(8)
C(3)···C(4)	0.068(8)
O(1)···O(2) $\left\{ \begin{array}{l} g \\ a \end{array} \right.$	0.161
	0.093
C(2)···C(4) $\left\{ \begin{array}{l} g \\ a \end{array} \right.$	0.148
C(1)···C(3) $\left\{ \begin{array}{l} g \\ a \end{array} \right.$	0.088
	0.204
O(1)···C(4) $\left\{ \begin{array}{l} gg \\ ga \end{array} \right.$	0.15
O(2)···C(1) $\left\{ \begin{array}{l} ga \\ aa \end{array} \right.$	0.111
C(1)···C(4)	0.324—0.128

a total of 27 combinations of dihedral angles are possible for 1,2-dimethoxyethane. Of these, however, some are identical and some are mirror images. This reduces the number of different conformers for 1,2-dimethoxyethane to ten: aaa , ag^+a , g^+aa , ag^+g^+ , ag^+g^- , g^+ag^+ , g^+ag^- , $g^+g^+g^+$, $g^+g^+g^-$ and $g^+g^-g^+$.

Of these, the $g^+g^+g^+$ conformers are unstable due to the repulsions because of the short interatomic distances between the methyl groups. This work therefore excludes these conformers. The sequence g^+g^- in the ag^+g^- and $g^+g^+g^-$ conformers, which results in high potential energies for the *n*-hexane, is found to be more favourable in 1,2-dimethoxyethane, where two CH_2 groups are exchanged with oxygen atoms. The multiplicity of the conformations are listed in Table 4.

Single conformers. In Fig. 5 is shown the conformation dependent part of the theoretical RD curves for the different conformers. Except for the $g^+g^+g^+$ and $g^+g^+g^-$ conformers (Fig. 5B) the rotamers do not show significant changes in the theoretical RD curves depending on the relative sign of two *gauche* dihedral angles. The bond distances and valence angles used in the calculations of the single conformers have been refined by a least-squares procedure (Table 1). The dihedral angles, however, had to be determined by trial and error.

Fig. 5 shows that it is impossible to obtain a

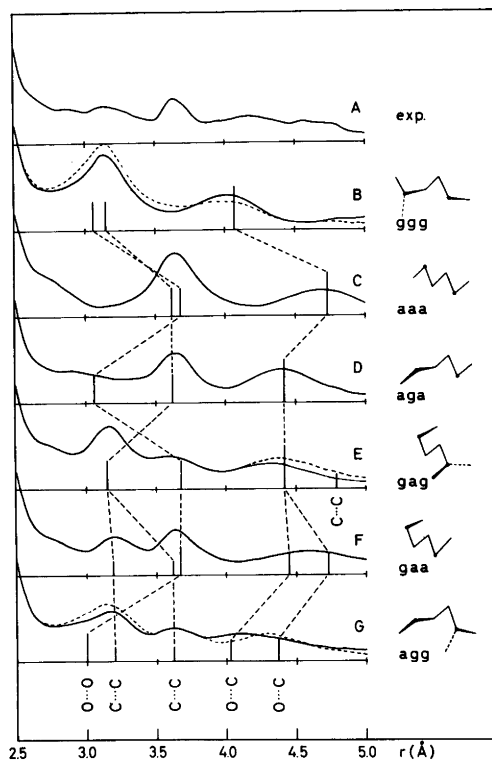


Fig. 5. 1,2-Dimethoxyethane. The outer part of the experimental (A) radial distribution curve compared with the corresponding part of theoretical radial distribution curves for the conformers $g^+g^+g^+$ ($g^+g^+g^-$) (B), aaa (C), ag^+a (D), g^+ag^+ (g^+ag^-) (E), g^+aa (F), and ag^+g^+ (ag^+g^-) (G). ($k=0.0022$ Å). The dotted curves correspond to the conformations in parentheses.

correspondence between the experimental data and the theoretical data for a single conformer in the gas phase.

Mixtures of two conformers. By comparison of the RD curves for the single conformations with the experimental RD curve, it may be seen that some conformers show too little area underneath the curve in regions where other conformers show too much. In the further analysis mixtures of two conformers were considered. The bond distances and the valence angles are assumed equal for all conformers, corresponding to the values determined for the single conformers, and are kept at fixed values during the analysis. The three dihedral angles for each conformer have been determined

by trial and error, as convergency could not be obtained by refinement of these parameters.

As shown in Fig. 5, curve B, E, and G, the differences between RD curves for two conformers that only differ by the relative sign of the *gauche* dihedral angles, are fairly small and cannot be told apart when several conformers appear. Therefore, the determined percentage of the conformers will represent the sum of g^+ and g^- conformations, and only conformers having g^+ angles have been included in the calculation of theoretical RD curves for the conformational mixtures. This reduces the number of different conformers to be handled in the calculations from nine ($g^\pm g^\mp g^\pm$ is excluded) to six: *aaa*, *aga*, *agg*, *gaa*, *gag* and *ggg*.

The *aaa* conformer, which has a too large peak at 3.6 Å and a too little area at 3.1 Å, needs to mix with conformers which have a larger area at 3.1 Å and a smaller at 3.6 Å in order to give satisfactory agreement with experimental data. Such conformers are *ggg*, *gag* or *agg*. (Fig. 6, curve (C+B), (C+E) and (C+G), respectively.)

Also the *aga* conformer has too large a peak at 3.6 Å and may therefore give satisfactory results when mixed with the *ggg*, *gag* or *agg* conformer (Fig. 6, curve (D+B), (D+E) and (D+G), respectively).

The *gaa* conformer corresponds fairly well to the experimental curve at 3.6 Å, but ought to mix with a conformer with a larger area at about 3.0 Å, such as *agg* and *gag*, in order to fit experimental data (Fig. 6, curve (F+G) and (F+E), respectively). The *ggg* conformer has too small an area at 3.6 Å, which in a mixture with *gaa* will give too small a peak.

In Fig. 6 are shown the eight combinations of two conformations which give fair agreement between experimental and theoretical curves. The percentage contributions of the conformers in mixture are shown in Table 3.

It should be noticed that in these mixtures all the different rotational isomers except $g^+g^-g^+$ are represented and hence according to the electron diffraction data, may exist in the gas phase. As any of the eight mixtures gives acceptable agreement between experimental and theoretical curves, also a mixture of any number of the eight mixtures will fit the experimental curve.

Mixtures of several conformers. From the theoretical calculations by Podo *et al.*¹³ it is concluded that nine different conformers of 1,2-dimethoxyethane should be present in the gas phase, although

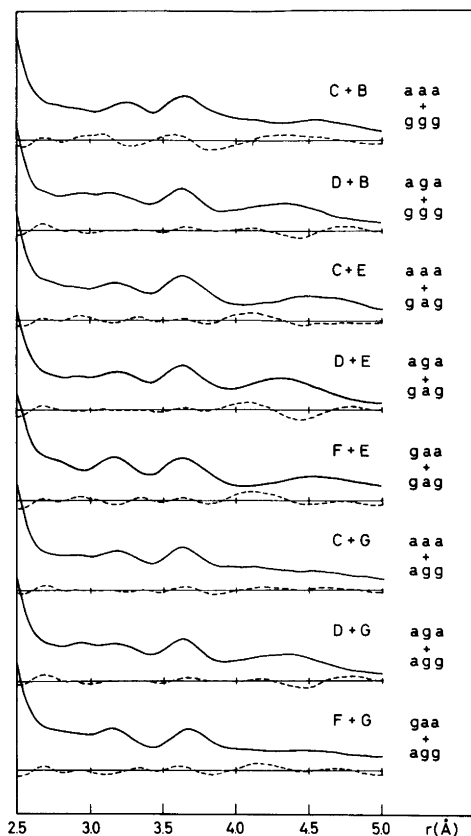


Fig. 6. 1,2-Dimethoxyethane. The outer part of the radial distribution curves for eight mixtures of two conformers, which give a satisfactory agreement between experimental and theoretical curves. The broken lines show the difference between experimental and theoretical values ($k=0.0022$ Å).

the populations of $g^+g^+g^+$, $g^-g^+g^+$, g^+ag^+ and g^-ag^+ are all smaller than 1.5% at room temperature. As may be seen from Table 4, the predominant conformers are calculated to be ag^+a and *aaa*, but also the *agg* (i.e. ag^+g^+ 13.1%, ag^-g^+ 5.8%) and the *gaa* (i.e. 16.0%) contribute considerably. A theoretical RD curve based on the geometrical parameters determined experimentally in this work and the population of the nine conformers calculated by Podo *et al.* is shown in Fig. 2 C. It may be seen that this percentage distribution shows too little area about 3.1 Å, corresponding to too small contribution from *gauche* dihedral angles, while the contribution at 3.6 Å and thereby the contribution from *anti* dihedral angles, is too large.

Table 3. Satisfactory agreement between experimental and theoretical data is obtained for the eight mixture of two conformations listed in the table below.

Mixture No.	Conformations	%
1	<i>aaa</i>	60(5)
	<i>+</i> <i>ggg</i>	40(5)
2	<i>aga</i>	75(5)
	<i>+</i> <i>ggg</i>	25(5)
3	<i>aaa</i>	46(5)
	<i>+</i> <i>gag</i>	54(5)
4	<i>aga</i>	64(6)
	<i>+</i> <i>gag</i>	36(6)
5	<i>gaa</i>	59(8)
	<i>+</i> <i>gag</i>	41(8)
6	<i>aaa</i>	28(7)
	<i>+</i> <i>agg</i>	72(7)
7	<i>aga</i>	50(7)
	<i>+</i> <i>agg</i>	50(7)
8	<i>gaa</i>	49(10)
	<i>+</i> <i>agg</i>	51(10)

To sum up, it seems reasonable to expect the conformational mixture of 1,2-dimethoxyethane to be composed of several conformers. The introduction of several conformers of unknown geometry and percentage contribution in the equilibrium mixture would include a very large number of independent parameters. As molecules in the gas phase are randomly oriented, the information of the molecular geometry from an electron diffraction experiment is one dimensional and only interatomic distances are determined. The determination of such a large number of independent parameters would then be a more or less impossible task.

Thus, in the further attempts to determine the percentage composition of the equilibrium mixture of 1,2-dimethoxyethane several parameters had to be kept at fixed values.

The bond distances and valence angles, which can be determined from the first four peaks in the RD curve, have been assumed equal for all conformers and have been determined by a least-squares refinement of the data. In the calculations of two-conformation mixtures these parameters have been kept at determined values, while the dihedral angles and percentage composition have been refined.

In the different conformers corresponding dihedral angles (*i.e.* CC–OC *anti*, CC–OC *gauche*, OC–CO *anti* and OC–CO *gauche*, respectively) have been found to deviate less than the standard deviations. Mean values for each of these dihedral angles have therefore been assumed to be correct for all relevant conformers. The contribution from the long C(1)··C(4) distances to the RD curve is negligible.

It may be seen from Table 1 that the CC–OC dihedral angles, *i.e.* 152.4 and 88.7°, deviate considerably from ideal *anti* and *gauche* angles, while

Table 4. The multiplicities and the percentage contribution of the six distinguishable conformers of 1,2-dimethoxyethane.

Conformation	Multiplicity	Percentage contribution Determined in this work	Calculated by Podo <i>et al.</i>
<i>aga</i>	2	23(7)	36.6
<i>aaa</i>	1	13(7)	23.9
<i>gaa</i>	4	3(7)	16.0
<i>agg</i> ^b	8	53(7)	18.9
<i>gag</i> ^b	4	5	2.7
<i>ggg</i> ^{b,a}	6	3	1.9

^a The multiplicity of the *ggg* conformer is reduced from 8 to 6, because the $g^+g^-g^+$ and $g^-g^+g^-$ are excluded.

^b Dihedral angles g^+ and g^- cannot be distinguished in the RD curve. Therefore the sum of these conformers are listed.

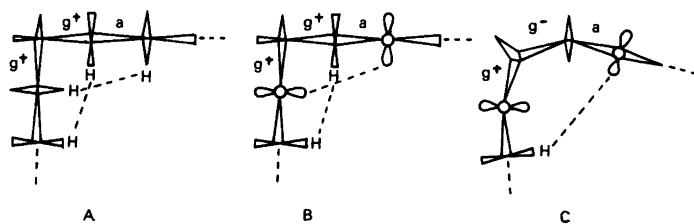


Fig. 7. Schematic drawing showing (A) the ag^+g^+ conformation and $H\cdots H$ interactions in cycloalkanes, (B) the ag^+g^+ conformation, $O\cdots O$ and $H\cdots H$ interactions in the 1,4-dioxo grouping, (C) the ag^-g^+ conformation and $O\cdots H$ interaction in the 1,4-dioxo grouping (Ref. 30).

the $OC-CO$ dihedral angles are close to ideal. This observation is consistent with what is found for some chemically related large rings, *i.e.* 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6)²⁸ and dibenzo-30-crown-10.²⁹ In the crystalline state the preferred conformation for the $C-O-C-C-O-C$ units at "corners" is reported to be ag^+g^+ , the dihedral angles being 155, -75, 80°, and 148, -67, 95°, respectively. These angles are in good agreement with the dihedral angles determined in this investigation, and suggest the presence of the ag^+g^+ conformer rather than the ag^+g^+ , which is the more stable for alkanes.

In a recent paper³⁰ the difference in the conformational situation for cycloalkanes and cyclic polyethers is explained as an exchange of unfavourable $H\cdots H$ interactions by more favourable $O\cdots H$ interactions. If the 1,4-dioxo system is incorporated in the unchanged cycloalkane conformation a *gauche* 1,4- $CH\cdots HC$ interaction (Fig. 7A) will be replaced by a 1,4- $O\cdots O$ interaction (Fig. 7B), which is probably not much better as the dipoles are parallel. By converting the ag^+g^+ unit to ag^+g^+ , the ether dipoles will not be parallel and a more favourable 1,5- $CH\cdots O$ interaction (Fig. 7C) may stabilize the system. From these arguments it seems reasonable to expect the ag^+g^+ conformer to be present also in the gas phase.

As only average *anti* and *gauche* dihedral angles are determined for all conformers, also the *aaa* and *aga* conformers are found to have these rather unusual $CC-OC$ angles. An attempt to keep the $CC-OC$ dihedral angles at 180.0° for the *aaa* and *aga* conformers resulted in a poorer correspondence between experimental and theoretical data. However, it is reasonable to believe that the different conformers have somewhat different valence and dihedral angles, and that shrinkage

effects are present, even if a determination of these parameters is not possible.

By keeping the bond distances, valence angles and dihedral angles at fixed values, attempts have been made to refine the population of the six conformers. In order to obtain convergency in the refinements also the population of some conformers had to be assumed. As the contribution of the g^+ag^+ , g^+ag^+ , $g^+g^+g^+$, and $g^+g^+g^+$ is calculated to be totally less than 5%,¹³ these conformers are assumed to contribute very little to the equilibrium mixture. In the refinement the percentages of these conformers have been kept at fixed values, the sum of which has been changed gradually from 0 to 20%. Independent of the contribution from the *gag* and *ggg* conformers, *agg* is found to be the predominant conformer in the mixture, but also the *aaa* and *aga* conformers contribute considerably. An increase of *gag* + *ggg* conformers from 0 to 20% results in a decrease of the *gaa* and *agg* conformers, and a small increase of the *aaa* and *aga* conformers. The contribution of the *gaa* conformer changes from 9 to 0% and for the *agg* conformer from 60 to 45%. At the same time the contribution of the *aga* conformer increases from 19 to 25% and the *aaa* conformer from 10 to 15%. The percentage distribution corresponding to the smallest sum of square residuals is listed in Table 4, the theoretical RD curve is shown in Fig. 2B.

The distribution of conformers with different energy in an equilibrium mixture will, of course, depend on temperature. The electron diffraction experiment has therefore been carried out at two temperatures, *i.e.* room temperature and 280 °C. However, no differences in the conformational population could be observed from the two sets of experimental data. Only a broadening of the peaks in the RD curve recorded at the higher tempera-

ture, is observed due to an increase in the mean vibrational amplitudes. This could be expected since several conformers exist in a mixture. The effect of a decrease of one conformer might well be compensated by the increase of another.

The width of the peaks in the RD curve are dependent on the vibrational amplitudes (u -values). As the peaks in the conformation-dependent part of the curve are not well-resolved, it is difficult to determine the u -values for the longer interatomic distances. These parameters have therefore been calculated in a normal coordinate analysis³¹ based on the force constants determined by Zerbi and Snyder.¹⁷ The resulting u -values are listed in Table 2.

Except for the already mentioned correlation between the C—C distance and the O—C distances ($\rho=0.68$) and for a correlation between the C—O distance and the vibrational amplitude of the C—C bond ($\rho=0.88$), the correlation between other refined parameters is small. It should, however, be mentioned that only a few u -values have been refined.

CONCLUSION

The conformational analysis of 1,2-dimethoxyethane in the gas phase does not result in an unequivocal solution to the problem. No single conformer gives a satisfactory agreement between experimental and theoretical data. It can therefore be concluded that 1,2-dimethoxyethane exists as a mixture of conformers in the gas phase. As a result of the electron diffraction analysis eight different mixtures of two conformers give a satisfactory agreement with the experimental curve. As these mixtures represent all the nine different conformers ($g^+g^+g^+$ are excluded), these conformers may in principle all be present in the gas phase equilibrium mixture.

The presence of several conformers of 1,2-dimethoxyethane has also been established by spectroscopic methods^{12,14-19,22} and dipole moment measurements^{20,21} in the liquid state and in solution. However, from these investigations there is some disagreement as to the number and types of conformers present, although all agree on *aga* and *aaa* being the most stable conformers. This is also in accordance with the theoretical analysis¹³ of 1,2-dimethoxyethane. It should be noticed that a satisfactory agreement between experimental elec-

tron diffraction curves and those of a mixture of the two most stable conformers *aga* and *aaa*, cannot be obtained. Thus, it seems reasonable that more than two conformers are present in the gas phase.

Based on the assumptions that several conformers are present in the gas phase and that the contribution of *gag* and *ggg* conformers is fairly small (according to the theoretical calculations¹³), the percentage composition has been determined. A composition of 13% *aaa*, 23% *aga*, 53% *agg*, 3% *gaa*, 5% *gag*, and 3% *ggg* is shown in Fig. 2B to be in good agreement with experimental data.

The rather unusual values observed for the *anti* and *gauche* CC—OC dihedral angles (Table 1) as average values for all the present conformers, are in good agreement with what is found for large ring systems,^{26,27} having C—O—C—C—O—C units.

As is seen from Table 4, the standard deviations of the determined percentage are fairly large, even though other independent parameters have been kept at fixed values. If all parameters could have been refined simultaneously still larger standard deviations should have been expected. The percentage contribution of the conformers determined here must, therefore, only be regarded as approximate values. It should, however, be noted that the conformations predominating in the mixture, correspond to those which have earlier been reported in the literature for the C—O—C—C—O—C unit. To the author's knowledge the *gaa*, *gag*, and *ggg* conformations have not been observed.

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