

The Molecular Structure of 2,2-Dimethoxypropane, $\text{CH}_3\text{—O—C}(\text{CH}_3)_2\text{—O—CH}_3$, in the Gas Phase

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The molecular structure of 2,2-dimethoxypropane has been investigated in the gas phase by the electron-diffraction method. The preferred conformation is found to be *gauche, gauche* with a C_2 symmetry. The dihedral angle, α (COC), is $52.0(1.2)^\circ$. The geometric parameters are: $r(\text{C—O}) = 1.423(6) \text{ \AA}$, $r(\text{C—C}) = 1.513(8) \text{ \AA}$, $r(\text{C—H}) = 1.104(8) \text{ \AA}$, $\angle\text{COC} = 114.0(1.4)^\circ$, $\angle\text{OCO} = 117.4(2.2)^\circ$, $\angle\text{CCO} = 112.2(2.9)^\circ$, $\angle\text{CCH} = 111.6(1.1)^\circ$, $\angle\text{OCH} = 107.8(1.3)^\circ$.

The structure of 2,2-dimethoxypropane (Fig. 1) was investigated in order to obtain information about the conformation of what may be looked upon as a unit-brick of larger ring systems, $-(\text{CH}_2-\text{O}-\text{C}(\text{CH}_3)_2-\text{O})_n-$. This structure determination is part of a study on cyclic and acyclic ethers.

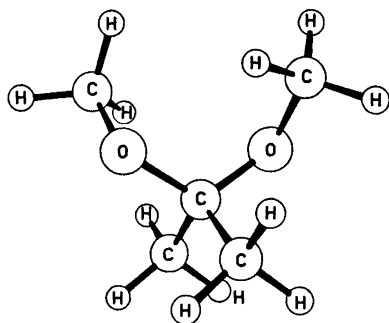


Fig. 1. 2,2 Dimethoxypropane.

Cumper¹⁻⁴ and co-workers have investigated a number of different methoxy compounds using electric dipole moment measurements and ultraviolet and NMR spectroscopic investigations. They conclude that in the $(\text{CH}_3)_{4-n}$ -

$\text{C}(\text{OCH}_3)_n$ derivatives only hindered rotation of the methoxy groups occurs. Calculations of the charge distributions for the mentioned methoxy derivatives have been performed by Nagy and Párkányi⁵ and correlated with NMR data.

EXPERIMENTAL

The electron diffraction diagrams of a commercial sample of 2,2-dimethoxypropane were taken on a Balzers Eldigraph KDG2 unit. The sample was kept at about 0°C during exposure. The background pressure during the experiment was approximately 1.5×10^{-5} Torr. The electron diffraction patterns were recorded at 25.00 and 50.00 cm nozzle-to-plate distances and the electron wavelengths were 0.05850 and 0.05852 \AA , respectively. For the structure analysis five plates for the 25 cm distance and four plates for the 50 cm distance were selected. 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.⁶ An experimental background was subtracted on each plate before averaging the intensity data. The molecular intensity curves from the 25 cm and 50 cm nozzle-to-plate distances were scaled and combined to one experimental molecular intensity curve extending from $s = 1.375 \text{ \AA}^{-1}$ to $s = 30.00 \text{ \AA}^{-1}$ (Fig. 2). The mean values were used in the overlap region. The intensity was modified by $s/|f_C| |f_O|$, where f' is the complex scattering factor^{7,8} for carbon and oxygen, respectively.

The distances and the vibrational amplitudes estimated from the experimental radial distribution (RD) curve were refined by a least-squares procedure. The calculations have been carried out on CDC 3300 and CDC 7400 (CYBER) computers.⁶

STRUCTURE ANALYSIS AND RESULTS

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

The bond distances in the molecule are represented by the two first peaks in the RD curve. The first peak at 1.1 Å corresponds to the C–H bond distances. All the C–H distances are assumed to be equal. The peak at 1.5 Å contains both the C–O and C–C bond distances. From the structure of related molecules, dimethoxymethane⁹ and tetramethoxymethane,¹⁰ a difference in the central and terminal C–O bond lengths should be expected. Unfortunately, in this investigation the correlations between the C–O and C–C bond distances and the corresponding vibrational amplitudes are so large that these parameters may not be determined with a great accuracy, and consequently only a mean C–O bond distance may be determined. At least two of the four mentioned parameters had to be kept at fixed values to give reasonable results during the refining procedure. Table 1 shows the parameter values from different refinements together with the errors of square residuals.

The next peak in the RD curve, at about 2.4 Å, contains information about the CCO, OCO, COC, and CCC bond angles. The main contributions to this peak are the four C···O distances

from the oxygen atoms in the methoxy groups to the methyl carbon atoms (2.36 Å), the O···O distance (2.43 Å), which corresponds to an OCO angle of 117.4°, the two C···C distances from methoxy carbons to the central carbon atom (2.39 Å) (\angle COC equal to 114.0°), and the C···C distances between the two methyl group carbon atoms (2.51 Å), corresponding to a CCC angle of 112.2°. The shoulder at about 2.0–2.2 Å shows the O···H distances in the methoxy groups and the C···H distances between the central carbon atom and the methyl hydrogen atoms. It is assumed that the CCC plane formed by the central carbon atom and the methyl carbon atoms is perpendicular to the OCO plane and bisecting the angle OCO.

The maxima determining the conformation of the molecule are the three well-resolved peaks in the outer part of the RD curve at 2.9, 3.3, and 3.7 Å. The first of these represents the C···O distances between non-bonded methoxy carbon and oxygen atoms (2.89 Å), and the two shorter C···C distances between methoxy and methyl carbon atoms (2.89 Å). The next peak corresponds to the C···C distances between the methoxy carbons (3.30 Å), and the last peak the two longer C···C distances between methoxy and methyl carbon atoms (3.67 Å).

The best agreement between experimental and theoretical curves is obtained for a *gauche*, *gauche* conformation of the C–O–C–O–C chain, the dihedral angle being 52.0°. A *gauche*,

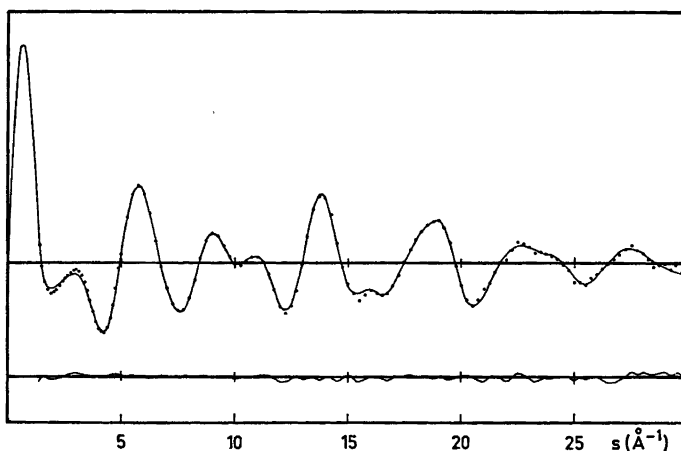


Fig. 2. 2,2-Dimethoxypropane. Theoretical (solid line), experimental (dots), and difference molecular intensity curve.

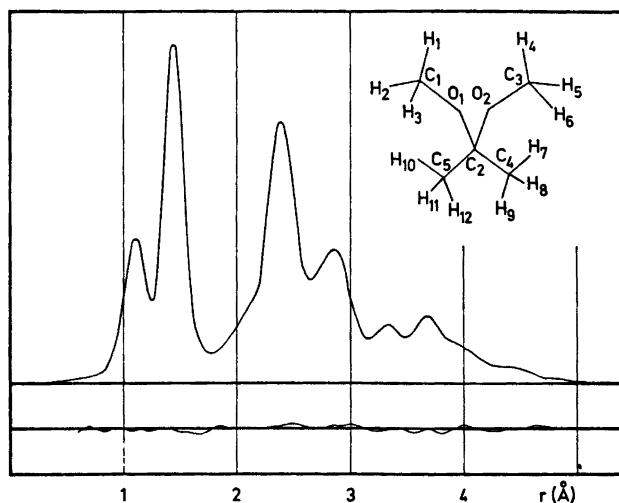


Fig. 3. 2,2-Dimethoxypropane. Theoretical radial distribution curve. The lower curve shows the difference between the experimental and the theoretical values. Artificial damping constant $k = 0.002 \text{ \AA}$.

Table 1. The results of different cycles of least-squares refinement of the parameters for the C–O and C–C bond distances and vibrational amplitudes. Σ shows the errors of square residuals for each cycle. Due to the large correlation of the listed parameters, only two of these could be refined simultaneously.

C–O <i>R</i>	<i>u</i>	C–C <i>R</i>	<i>u</i> ^a	Σ
1.41 ^a	0.051(7)	1.508(16)	0.050	483.8
1.425(6)	0.048 ^a	1.506(9)	0.050	113.0
1.425(6)	0.046 ^a	1.510(9)	0.050	111.8
1.424(6)	0.044 ^a	1.513(8)	0.050	113.8
1.424(6)	0.046 ^a	1.510(8)	0.048	110.9
1.424(6)	0.046 ^a	1.510(8)	0.046	110.3
1.423(6)	0.046 ^a	1.510(8)	0.044	110.2
1.423(6)	0.045 ^a	1.513(8)	0.044	107.2
1.423(6)	0.044 ^a	1.514(8)	0.044	109.0

^a Values kept fixed during the refinement.

gauche conformation could be expected because the lone pair interaction in this conformation should be more favourable than in an all-*anti* conformation. The angle OCO is found to be 117.4° and the angle COC to be 114.0° . The latter is in good agreement with the corresponding angle in the cyclic ether 1,3,5-trimethyltrioxan,¹¹ and the acyclic dimethoxymethane⁹

and tetramethoxymethane.¹⁰ The OCO angle found in this molecule is, however, somewhat larger than those found in the other ethers mentioned above.

In both dimethoxymethane and 2,2-dimethoxypropane are the shortest O···H distances, which extend over more than one angle, fairly small, 2.09 and 2.34 Å, respectively. This is a fact which may indicate an interaction between oxygen and hydrogen atoms. Also the C–C bond distances in this molecule are found to be shorter (1.513 Å) than what is usually found for such bonds. It should be mentioned that a shorter C–C bond distance (1.49 Å) also is found in 1,3,5-trimethyltrioxan.

The twist of the CH₃ groups about the C–C and C–O bonds cannot be determined with great accuracy because of the poor scattering power of hydrogen atoms. It was assumed that the two methyl groups had an equal twist, and the best result was obtained for an ideal staggered conformation. The twist of the methoxy CH₃ groups were also assumed to be equal and refined to 15.9° from an ideal staggered position.

As already mentioned, the refinement of the C–O and C–C bond distances and their vibrational amplitudes may not be carried out simultaneously because of the great correla-

Table 2. Structure parameters for 2,2-dimethoxypropane obtained by least-squares refinement on the intensity data. 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	1.423(6)	0.045
C—C	1.513(8)	0.044
C—H	1.104(8)	0.070(04)
O ₁ ···O ₂	2.432(21)	0.064(15)
C ₄ ···O ₂	2.359(12)	0.079
C ₁ ···O ₂	2.885(12)	0.110(11)
C ₁ ···C ₂	2.388(16)	0.073(09)
C ₄ ···C ₂	2.512(36)	0.078
C ₁ ···C ₄	2.886(18)	0.108
C ₁ ···C ₃	3.303(31)	0.120
C ₁ ···C ₅	3.671(8)	0.128(12)
O ₁ ···H ₁	2.038(16)	0.091(18)
O ₁ ···H ₆	2.337(29)	0.120
O ₁ ···H ₅	2.611(17)	
O ₁ ···H ₉	2.662(24)	0.116
O ₁ ···H ₇		
O ₁ ···H ₄	3.526(41)	
O ₁ ···H ₅	3.705(31)	0.122
C ₂ ···H ₇	2.177(14)	0.093
C ₁ ···H ₆	2.891(56)	0.148
C ₁ ···H ₄	3.510(53)	0.156
C ₁ ···H ₇	3.953(28)	0.120
C ₁ ···H ₅	3.997(17)	0.120
C ₁ ···H ₃	4.336(35)	0.160
C ₁ ···H ₉	4.537(16)	0.132
H ₁ ···H ₆	1.782(14)	0.094
H ₁ ···H ₂	1.831(12)	
H ₁ ···H ₄	4.597(48)	0.20
Angles		deg.
∠COC		114.0(1.4)
∠OCO		117.4(2.2)
α(CH ₃ O) ^a		52.0(1.2)
∠OCH		107.8(1.3)
τ(CH ₃) ^b		15.9(2.1)
∠CCC		112.2(2.9)
∠CCH		111.6(1.1)

^a α is the twist angle of the methoxy groups around the central CO bonds. (Dihedral angle C—O—C—O). ^b τ is the twist angle of the CH₃ in the methoxy groups around the terminal CO bonds.

tions. Two of these parameters were kept at fixed values during the refinements. If the vibrational amplitudes are fixed at reasonable values, the C—C and the C—O distances may be refined simultaneously with the COC, OCO, CCC, OCH, and CCH angles, the twist

angles of the CH₃—O— groups and the methoxy CH₃ groups, and the vibrational amplitudes for O···O and the shorter O···H non-bonded distances. As the correlation between the COC and CCC angles is considerable (0.8), the vibrational amplitudes for the C···C and C···O distances have been refined in separate cycles. The remaining vibrational amplitudes have been grouped according to distance type and lengths and refined in separate cycles. Keeping some parameters at fixed values during the refinements results in too small standard deviations for some of the parameters. To compensate for this, the approach proposed by Seip,¹⁵ has been applied to some of the most important parameters. The final parameters are shown in Table 2 and the correlation matrix in Table 3.

CONCLUSION

As expected the conformation of 2,2-dimethoxypropane is found to correspond to that of dimethoxymethane, i.e. +*gauche*, +*gauche*. Due to substitution of hydrogen atoms by the much larger CH₃ groups the angles in 2,2-dimethoxypropane are generally somewhat larger than the corresponding angles in dimethoxymethane⁹ and the dihedral angle of the C—O—C—O—C chain somewhat smaller (52 and 63°, respectively), giving more space to the methyl groups. The bond distances are found to be close to what is usually found for distances of this type. The shortest non-bonded O₁···H₅ distance is, however, found to be somewhat short, and this may indicate that a weak oxygen-hydrogen interaction is present.

Dipole moment measurements show that 2,2-dimethoxypropane possesses a small dipole moment, as is also found for dimethoxymethane (0.61 D¹² and 0.99 D,⁹ respectively). By comparison¹² of these moments with that of a compound having a +*gauche*, -*gauche* conformation of the C—O—C—O—C skeleton (e.g. 1,3-dioxan) it is seen that the latter has a considerably greater dipole moment (1.9 D¹³). Dipole moments for the *gauche,anti* and *anti,anti* conformations should be expected to be still larger.

Calculations of dipole moments¹ according to Eyring,¹⁴ has been carried out for different

Table 3. Correlation matrix ($\times 100$) for the parameters. (The coefficients having absolute values less than 20 are not given.)

Parameters	1	2	3	4	5	6	7	8	9	10	11	12
1 $r(C_1-O_1)$	100											
2 $\angle COC$		100										
3 $\angle OCO$		-87	100									
4 $\alpha(CH_2O)^a$			38	100								
5 $\angle OCH$					100							
6 $\tau(CH_3)^b$		42	-27			100						
7 $r(C_2-C_6)$	-24	-34	30			-28	100					
8 $\angle CCC$		86	-86	-28		24		100				
9 $\angle CCH$		-33	39			-31		-43	100			
10 $u(O_1 \cdots O_2)$		-30	24			23		-78		100		
11 $u(O_1 \cdots H_1)$		37	-53		21		-21	30	-65		100	
12 scale	-24	-22	26		-24	-29	59				-21	100

^a α is the twist angle of the methoxy groups around the central CO bonds. ^b τ is the twist angle of the CH_3 in the methoxy groups around the terminal CO bonds.

conformers of the molecule. The best agreement with the measured dipole moment is obtained for a dihedral angle of 77° , which is in good agreement with the result of this work.

Acknowledgement. We are grateful to Mr. K. Brendhaugen for his assistance during the experiment.

14. Eyring, H. *Phys. Rev.* 39 (1932) 746.
 15. Seip, H. M. *A Specialist Periodical Report: Molecular Structure by Diffraction Methods*, The Chemical Society, London 1973, Vol. 1, p. 53.

Received May 16, 1975.

REFERENCES

- Cumper, C. W. N., Melnikoff, A. and Vogel, A. I. *J. Chem. Soc. A* (1966) 323.
- Cumper, C. W. N. and Rossiter, R. F. *J. Phys. Chem.* 76 (1972) 525.
- Cumper, C. W. N., Melnikoff, A. and Vogel, A. I. *J. Chem. Soc. A* (1966) 242.
- Cumper, C. W. N., Melnikoff, A., Mooney, E. F. and Vogel, A. I. *J. Chem. Soc. B* (1966) 874.
- Nagy, J. and Párkányi, L. *Acta Chim. (Budapest)* 71 (1972) 159.
- Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
- Peacher, J. and Wills, J. C. *J. Chem. Phys.* 46 (1967) 4809.
- Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* 40 (1964) 1686.
- Astrup, E. E. *Acta Chem. Scand.* 27 (1973) 3271.
- Mijlhoff, F. C., Geise, H. J. and van Schaick, E. J. M. *J. Mol. Struct.* 20 (1973) 393.
- Astrup, E. E. *Acta Chem. Scand.* 27 (1973) 1345.
- Dale, J. and Ekeland, T. *Acta Chem. Scand.* 27 (1973) 1519.
- Arbousow, B. A. *Bull. Soc. Chim. Fr.* (1960) 1311.