The Molecular Structure of Dimethoxymethane, CH₃-O-CH₂-O-CH₃, in the Gas Phase

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The molecular structure of dimethoxymethane (methylal) has been investigated in the gas phase by the electron diffraction method. The molecule has a C_2 symmetry and the preferred conformation is found to be *gauche-gauche*. The dihedral angle, $\delta(COCO)$, is 63.3°. The most important parameters are as follows: $r(C-O)_{term.} = 1.432$ (0.004) Å, $r(C-O)_{centr.} = 1.382$ (0.004) Å, $r(C-H) = 1.108$ (0.004) Å, $\angle COC = 114.6$ (0.5)°, $\angle OCO = 114.3$ (0.7)°, $\angle OCH = 110.3$ (0.6)°.

The structure of dimethoxymethane was investigated as part of a study of cyclic[1] and acyclic ethers. A short communication[2] reporting the preliminary results of this work was published in 1971. Dimethoxymethane has previously been investigated, using the electron diffraction technique by Donohue[3] in 1950, by Aoki[4] in 1953, and recently by Andreassen and Bauer.[5] Donohue's work has not been published, but according to the quoted results he apparently assumed a planar all-*anti* conformation. Based on dipole moment
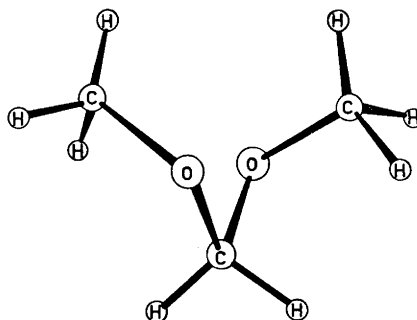

Fig. 1. Dimethoxymethane.

measurements[6] Aoki assumed that the most probable conformation should be the one having the two methyl groups located on opposite sides of the OCO plane. Aoki's electron diffraction investigation was based on visually estimated intensity data. The recent work of Andreassen and Bauer is in good agreement with the present work (Table 3).

Table 1. Structure parameters for dimethoxymethane 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_1-O_1(term.)	1.432	(0.004) ⎫	0.052	
C_2-O_1(centr.)	1.382	(0.004) ⎭		
$C-H$	1.108	(0.004)	0.063	(0.004)
$O_1\cdots O_2$	2.320	(0.017)	0.072	
$C_1\cdots O_2$	2.877	(0.012)	0.111	(0.013)
$C_1\cdots C_2$	2.366	(0.012)	0.066	(0.012)
$C_1\cdots C_3$	3.550	(0.033)	0.138	
$O_1\cdots H_1$	2.023	(0.007)	0.085	
$O_1\cdots H_6$	2.092	(0.014)	0.103	(0.016)
$O_1\cdots H_5$	2.477	(0.026)	0.112	
$O_1\cdots H_4$	3.520	(0.030) ⎫	0.121	
$O_1\cdots H_3$	3.737	(0.026) ⎭		
$C_2\cdots H_5$	2.525	(0.023)	0.110	
$C_1\cdots H_5$	3.175	(0.048)	0.130	
$C_1\cdots H_1$	3.306	(0.011)	0.098	
$C_1\cdots H_3$	4.093	(0.041) ⎫	0.130	
$C_1\cdots H_4$	4.451	(0.027) ⎭		
$H_3\cdots H_4$	1.799	(0.014)		
$H_1\cdots H_2$	1.810	(0.006)		
$H_5\cdots H_8$	2.596	(0.043)		
$H_2\cdots H_5$	3.585	(0.018)		

Angles	deg.	
∠ COC	114.6	(0.5)
∠ OCO	114.3	(0.7)
α(methoxy)[a]	116.7	(0.9)
∠ OCH	110.3	(0.6)
τ(CH$_3$)[b]	19.8	(2.0)
δ(COCO)[c]	63.3	(0.9)

[a] α is the twist angle of the methoxy groups about the central CO bonds. [b] τ is the twist angle of the methyl groups about the terminal CO bonds. [c] δ(COCO) is the dihedral angle of the carbon-oxygen chain.

EXPERIMENTAL

The electron diffraction diagrams of a commercial sample of dimethoxymethane were taken on a Balzer Eldigraph KDG-2. The sample was kept at approximately $-18°C$, and the electron wavelength was 0.05843 Å. The pressure in the apparatus during exposure was about 2×10^{-5} torr. Four plates were selected from each nozzle-to-plate distance, 25 cm and 50 cm, respectively. The intensity was recorded on a photometer for each 0.25 mm on the photographic plates. Each plate was oscillated about the centre of the diffraction diagram, and the intensity integrated over the arc. The data were treated the usual

Table 2. Correlation matrix (× 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	13
1 $r(C_1-O_2)$	100												
2 $r(C-H)$	−20	100											
3 ∠ COC			100										
4 ∠ OCO			−84	100									
5 $\alpha(CH_3O)^a$			−39	63	100								
6 $r(C_2-O_1)$	−76		−22			100							
7 ∠ OCH			−36	55	38		100						
8 $\tau(CH_3)^b$			−21		−21			100					
9 u_{C-H}	−20					32			100				
10 $u_{C_1\cdots C_2}$			−77	80	58	28				100			
11 $u_{C_2\cdots O_1}$									−38		100		
12 $u_{O_1\cdots H_4}$			20									100	
13 scale	52					51							100

a α is the twist angle of the methoxy groups about the central CO bonds. *b* τ is the twist angle of the methyl groups about the terminal CO bonds.

Table 3. Comparison of parameters for dimethoxymethane studied by electron diffraction.

Parameters	This study			Andreassen and Bauer [5]	
$r(C-O)_{term.}$	1.432	(0.004) Å		1.413	(0.003) Å
$r(C-O)_{centr.}$	1.382	(0.004) Å			
$r(C-H)$	1.108	(0.004) Å		1.119	(0.013) Å
∠ COC	114.6	(0.5)°		111.9	(3.6)°
∠ OCO	114.3	(0.7)°		114.0	(3.5)°
∠ OCH	110.3	(0.6)°		109.6	(2.2)°
$\delta(COCO)$	63.3	(0.9)°		61.8	(2.9)°

way.[7] The average curves from each nozzle-to-plate distance were combined to give one intensity curve covering an s-range of $1.75-29.25$ Å^{-1}. The intensity curve, modified by $s/|f_C||f_O|$, where f is the complex scattering factor for carbon and oxygen, is presented in Fig. 2.

The distances and vibrational amplitudes estimated from the RD (radial distribution) curve were refined by a least-squares procedure. The calculations have been carried out on a CDC 3300 computer.[8]

STRUCTURE ANALYSIS AND RESULTS

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

The two first peaks at about 1.1 Å and 1.4 Å on the RD curve represent the C−H and C−O bond distances, respectively. Attempts have been made to
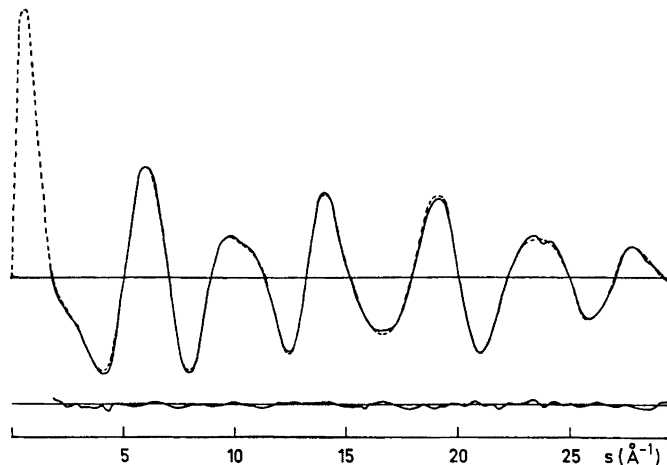
Fig. 2. Dimethoxymethane. Experimental (solid line), theoretical (dotted line), and difference molecular intensity curve.
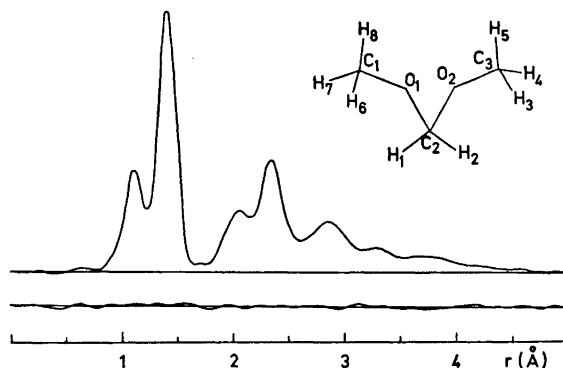

Fig. 3. Dimethoxymethane. Experimental radial distribution curve. The lower curve shows the difference between the experimental and the theoretical values. Artificial damping constant $k = 0.002$ Å.

determine whether there is only one $C-O$ bond length (model I) or different lengths of the terminal and central $C-O$ bonds (model II). The least-squares refinement of model I gives a $C-O$ bond distance of 1.405 Å and a corresponding vibrational amplitude (u-value) of 0.058 Å. This amplitude is somewhat greater than what has been found for $C-O$ bonds in other electron-diffraction investigations of ethers.[1, 13] However, the peak in question may consist of a sum of contributions from two slightly different bond lengths, which have smaller u-values than obtained for one average $C-O$ bond. A least-squares

refinement of two different $C-O$ bond lengths (model II) and their u-values do not converge, apparently because of the great correlation between these parameters. If the u-values of the two distances are assumed equal, they may be refined simultaneously with the two bond lengths, keeping all other parameters fixed. This gives a u-value of the $C-O$ distances of 0.052 Å, which is the same as the one found in 1,2-dimethoxyethane.[12] Subsequent refinements of the structure were performed by keeping this u-value fixed and refining the other parameters. The final result for the $C-O$ bonds is $r(C-O)_{terminal} = 1.432$ Å and $r(C-O)_{central} = 1.382$ Å. It should be mentioned that the correlation between the two $C-O$ bonds and their u-values makes the bond lengths much dependent of the determined vibrational amplitude. The refinements of the last-mentioned structure model (model II) gives the best fit between the experimental and the theoretical curves obtained in this investigation. One can not conclude unequivocally from these refinements that there are two different carbon-oxygen bond lengths in dimethoxymethane, however, the results indicate that this is the case.

The main contribution to the peak at $2.0-2.1$ Å is from $O\cdots H$ distances between oxygen atoms and hydrogen atoms in β-positions. The HCH plane of the methylene group is assumed to be perpendicular to the OCO plane and bisecting the angle OCO. The angle HCH in the methylene group is put equal to the tetrahedral angle, 109°28'. The angle OCH in the methoxy groups is determined to be 110.3°.

The best agreement between experimental and theoretical curves is obtained for the $\angle$OCO equal to 114.3° and the $\angle$COC equal to 114.6°. These angles do not differ much from what is found in the cyclic ether 1,3,5-trimethyl-trioxan,[1] though the OCO angle is found to be the greater in the latter compound. There is, however, a considerable correlation between these valence angles, and the determined difference is not significant.

The next peak in the RD curve at $2.3-2.4$ Å contains contributions from the $O_1\cdots O_2$ distance and the two $C_1\cdots C_2$ distances, being 2.320 Å and 2.366 Å, respectively.

The most significant peak for the determination of the conformation is found in the outer part of the RD curve at 2.9 Å. This peak contains contributions from $C_1\cdots O_2$ and $C_3\cdots O_1$ distances. The expected unfavourable interaction of lone pair electrons on the oxygen atoms in an all-*anti* conformation should be expected to favour a *gauche-gauche* conformation. This is also consistent with the result of this work. One methyl group is twisted above the OCO plane and the other methyl group below the plane. Convergence of the least-squares analysis could not be obtained in refinements where the two twist angles were refined simultaneously. Assuming equal twist angles for the two methyl groups about the central $C-O$ bonds resulted in a good fit between the experimental and the theoretical curves. The distances $C_1\cdots O_2$ and $C_3\cdots O_1$ are then equal, and the obtained u-values of 0.111 Å do not deviate from what could be expected for such a distance. Consequently it is reasonable to assume only one twist angle of the methoxy groups. The methoxy groups are found to be twisted 116.7° from an all-*anti* conformation, resulting in a dihedral angle, δ(COCO), of 63.3°.

The following independent parameters were simultaneously refined: $C-O$(terminal), $C-O$(central), $C-H$, $\angle COC$, $\angle OCO$, the twist angle $\tau(CH_3O)$ of the methyl groups about the central $C-O$ bonds, $\angle OCH(CH_3)$, the twist angle $\tau(CH_3)$ of the methyl groups about the terminal $C-O$ bonds, the mean amplitudes of vibration for the $C-H$ bond distances, the $C_1 \cdots C_2$, the $C_1 \cdots O_2$, and the $O \cdots H$ distances from the oxygen atoms to the methylene hydrogen atoms. The remaining vibrational amplitudes were grouped according to distance types and lengths, and were partly refined in separate cycles, partly assigned reasonable values, so that the sum of square residuals converge to the lowest value.

The vibrational amplitude for the $C-H$ bonds are found to be smaller in this work than usually found. This parameter is only slightly correlated with other parameters and will be of little importance for the over-all result.

The dipole moment of dimethoxymethane in benzene, measured by Krane,[9] is found to be 0.99 D. A simple calculation of the dipole moment is carried out, assuming each oxygen atom to have a dipole moment of 1.2 D. The resultant dipole moment is found to be 1.08 D. Dipole moments of some related ethers referred in the literature [10] are: dimethylether 1.30 D, methoxymethane 1.23 D, diethylether 1.15 D. As can be seen the dipole moment is not much influenced by the increasing chain length. The agreement between the experimental and the calculated value is satisfactory.

The dimethoxymethane may be looked upon as the unit element of the polyoxymethylene chain $(-CH_2-O-)_n$. Polyoxymethylene is reported to have a *gauche-gauche-gauche* conformation and the internal rotation angle is found to be about $77-78°$. In an X-ray investigation by Tadokoro *et al.*[11] the following bond lengths and angles (which are of interest to compare) have been found: $r(C-O)=1.42$ Å, $\angle OCO=110.8°$, $\angle COC=112.4°$, and the internal rotation angle $78.2°$. These values are in satisfactory agreement with the results obtained in this work.

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