

The Molecular Structure of 2,4,6-Trimethyl-trioxan (Paraldehyde)

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The molecular structure of 2,4,6-trimethyl-trioxan in the gas phase has been investigated by electron diffraction. The ring is found to have a chair conformation, and the three methyl groups are in equatorial positions. The most important molecular parameters are as follows: $r(\text{C}-\text{O}) = 1.410$ (0.004) Å, $r(\text{C}-\text{C}) = 1.494$ (0.009) Å, $r(\text{C}-\text{H}) = 1.104$ (0.007) Å, $\angle \text{COC} = 112.3$ (0.8)°, $\angle \text{OCO} = 110.7$ (0.7)°, $\angle \text{O}_1\text{C}_1\text{C}_2 = 109.2$ (1.0)°, $\angle \text{C}_3\text{C}_4\text{H}_5 = 110.7$ (1.3)°; the dihedral angle of the ring, $\delta(\text{OCOC})$, is found to be 54.6 (1.2)°.

The structure investigation of 2,4,6-trimethyl-trioxan has been carried out as part of a study on cyclic and acyclic ethers.

The structure of 2,4,6-trimethyl-trioxan has earlier been studied by electron diffraction by Ackermann and Mayer¹ in 1936, by Carpenter and Brockway²

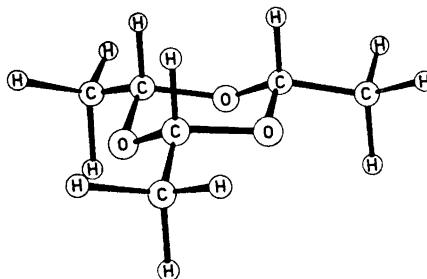


Fig. 1. 2,4,6-Trimethyl-trioxan.

in 1936, and by Aoki³ in 1953. These investigations were all based on visually estimated intensity data and the authors express doubt as to whether the compound contained a pure *e,e,e* conformation or a mixture of two isomers.

The sample of 2,4,6-trimethyl-trioxan used in the experiment was kindly supplied by J. Krane.⁴ The synthesis gives a mixture of the *e,e,e* and the *e,e,a* isomers and the two have been separated on a preparative gas chromatograph. The purity of the separated *e,e,e* sample was checked in the NMR spectrum

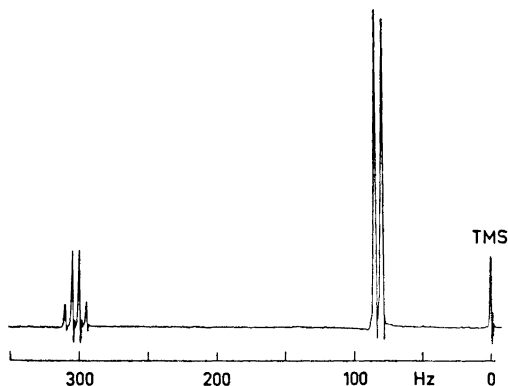


Fig. 2. NMR spectrum of 2,4,6-trimethyl-trioxan, showing the presence of a pure *e,e,e* conformation.

(Fig. 2). The spectrum shows one quartet due to the C-H protons and one doublet caused by the CH₃ protons. The spectrum shows no change with decreasing temperature. The chemical shift relative to TMS is 83 Hz for the CH₃ protons and 302 Hz for the C-H protons.

EXPERIMENTAL

Electron diffraction diagrams were taken on a Balzers Eldigraph KDG2. The nozzle temperature was about 23°C, and the electron wave length 0.05847 Å. The nozzle-to-plate distances were 50 and 25 cm. The pressure in the apparatus during exposure was 3×10^{-6} mmHg. Five selected plates were used for each distance. The intensity was recorded on a photometer for each 0.25 mm on the photographic plate. The plates were oscillated about the centre of each plate and the data integrated over the arc. The data were treated the usual way.⁵ The experimental background was subtracted on each plate before averaging the intensity data. The molecular intensity curves from the 50 cm plates and the 25 cm plates were scaled, and the mean values were used in the overlap region. The final intensity curve, shown in Fig. 3, extends from $s = 1.75 \text{ \AA}^{-1}$ to $s = 29.25 \text{ \AA}^{-1}$.

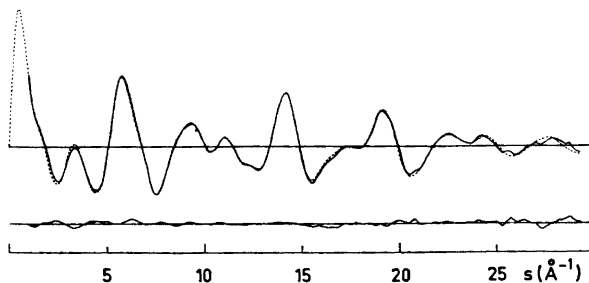


Fig. 3. 2,4,6-Trimethyl-trioxan. Experimental (solid line), theoretical (dotted line), and difference molecular intensity curve.

The modified molecular intensity may be expressed by the equation

$$I(s) = \text{const.} \sum_{i \neq j} g_{ij/mn}(s) \exp(-\frac{1}{2} u_{ij}^2 s^2) [(\sin r_{ij}s)/r_{ij}]$$

where

$$g_{ij/mn}(s) = \frac{|f_i| |f_j|}{|f_m| |f_n|} \cos(\Delta n_{ij})$$

In this case f_m was put equal to the complex scattering factor for carbon and f_n equal to the oxygen scattering factor to obtain a Gaussian shape of the carbon-oxygen peaks in the RD (radial distribution) curve.

The distances and u -values (vibrational amplitudes) estimated from the RD curve were refined by a least squares procedure. The numerical calculations have been carried out on a CDC 3300 computer.⁶

STRUCTURE ANALYSIS AND RESULTS

Approximate values for the molecular parameters, which were used in the least squares analysis of the structure, were determined from the experimental RD curve (Fig. 4).

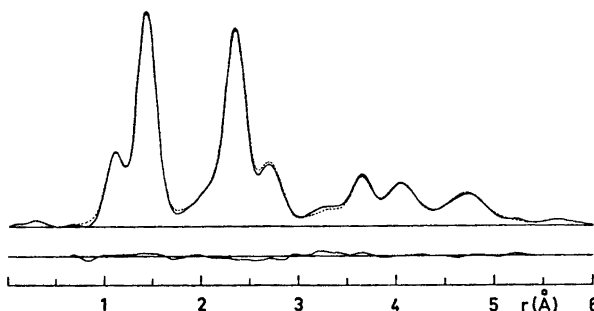


Fig. 4. 2,4,6-Trimethyl-trioxan. Experimental (solid line), theoretical (dotted line), and difference radial distribution curve. The damping constant is equal to 0.002 \AA^2 .

There is no indication from the RD curve that a contribution from the a,a,a conformation is present. This is as expected since the energy of this conformation must be much higher than for the e,e,e conformation because of the methyl-methyl interaction in axial positions.

The bond distances in the molecule are found in the two first peaks in the RD curve. At about 1.1 \AA is the peak corresponding to the C-H bond distances, and the C-O and the C-C bond distances contribute to the peak at $1.3 - 1.6 \text{ \AA}$. The C-O bond lengths are determined to be about 1.41 \AA , as found in other ethers,^{7,8} and the C-C bond length 1.49 \AA , which is slightly shorter than expected. The peak at 2.3 \AA is composed of C...O distances from the ring oxygen atoms to the nearest methyl carbon atoms and O...O and C...C distances in the ring. The main contribution to the peak at 2.7 \AA is from the C...O distances in the ring. The C...C distances from the carbon atoms in the ring to the methyl carbon atoms must be expected to occur at 3.6 \AA , the long C...O distances from the oxygen atoms to the methyl carbon at 4.0 \AA , and the C...C distances

between the methyl carbon atoms at 4.7 Å, which explains the three well resolved outer peaks on the RD curve.

The C-H axial bond distances are assumed to be parallel to the threefold axis. This assumption may not be quite correct and may be responsible for some minor discrepancies between the experimental and the theoretical curves. But because of the insignificant contribution of the distances containing these hydrogen atoms to the RD curve, their exact positions are difficult to determine. An attempt was made to determine a possible difference between the C-H bond distances in the methyl groups and the axial C-H bond distances in the ring, but no difference could be determined.

The position and the shape of the peak at 2.7 Å is sensitive to a twist of the methyl groups about the C-C bonds. A twist angle, $\tau(\text{CH}_3)$, of approximately $10-11^\circ$ from an ideal staggered position of the methyl hydrogen atoms with respect to the axial C-H bonds gives a better fit between the experimental and the theoretical RD curve for this peak than is obtained for an ideal staggered conformation, but less good for the peak at 2.3 Å and 3.6 Å. The lowest sum of square residuals in the least squares refinement is obtained for the exact staggered conformation.

The following independent molecular parameters were simultaneously refined (Fig. 5): C-O, C-C, C-H, α (the angle between the $\text{O}_1\text{C}_1\text{C}_5$ plane and

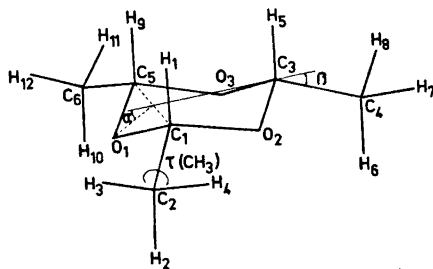


Fig. 5. The symbols and numbering system used for the 2,4,6-trimethyl-trioxan model.

the plane through $\text{C}_1\text{C}_3\text{C}_5$), β (the angle between the plane $\text{C}_1\text{C}_3\text{C}_5$ and $\text{C}_3\text{-C}_4$), $\angle \text{C}_3\text{C}_4\text{H}_6$, and the vibrational amplitudes for the bond distances C-O and C-H and for the non-bonded distances O...C and the C...C between the methyl carbon atoms. The remaining u -values were grouped according to distance type and length. The values for the remaining non-bonded O...H and C...H distances were obtained from separate cycles of refinement, while the amplitudes for the non-bonded H...H distances were fixed at reasonable values.

The least squares refinement converges to the results listed in Table 1. The u -values found for the C-H bond distances are smaller than what is usually found for C-H bonds. From the correlation matrix (Table 2) it is seen that the C-H amplitude of vibration is only slightly correlated with the other parameters, and consequently this amplitude will hardly influence the overall result.

In Table 3 is shown a comparison of the ring angles OCO and COC in 2,4,6-trimethyl-trioxan and in different investigations of 1,3,5-trioxan. In the

Table 1. Structure parameters for 2,4,6-trimethyl-trioxan 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 atoms, see Fig. 5.)

Distances	r		u	
C ₁ -O ₁	1.410	(0.004)	0.057	(0.005)
C ₁ -C ₂	1.494	(0.009)	0.052	(0.005)
C-H	1.104	(0.007)	0.051	(0.009)
O ₁ ...O ₂	2.319	(0.012)	0.067	(0.006)
C ₂ ...O ₁	2.366	(0.008)	0.065	(0.009)
C ₃ ...O ₁	2.723	(0.008)	0.081	(0.014)
C ₄ ...O ₁	4.067	(0.009)	0.108	(0.025)
C ₁ ...C ₅	2.341	(0.015)	0.076	(0.007)
C ₁ ...C ₄	3.644	(0.005)	0.087	(0.010)
C ₂ ...C ₄	4.719	(0.014)	0.101	(0.040)
C ₃ ...H ₅	2.146	(0.018)	0.109	
C ₃ ...H ₁	2.587	(0.012)	0.140	
C ₂ ...H ₁	2.175	(0.015)	0.074	
Angles				
∠C ₅ O ₁ C ₁	112.3	(0.8)		
∠O ₁ C ₁ O ₂	110.7	(0.7)		
α	32.4	(1.0)		
β	23.1	(1.6)		
τ(CH ₃)	0.0			
δ(OCOC)	54.6	(1.2)		
∠O ₁ C ₁ C ₂	109.2	(1.0)		
∠C ₂ C ₁ H ₁	113.1			
∠O ₂ C ₁ H ₁	107.4			
∠C ₃ C ₄ H ₅	110.7	(1.3)		

Table 2. 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	13	14
1 $r(\text{C-O})$	100													
2 $r(\text{C}_1\cdots\text{C}_5)$		100												
3 $r(\text{C-C})$	-40	-39	100											
4 $r(\text{C-H})$			29	100										
5 α	38	-20			100									
6 β	-20	51	41		-69	100								
7 ∠C ₃ C ₄ H ₅							100							
8 $u_{\text{C-O}}$	32	36	-89	-32		-37		100						
9 $u_{\text{C-H}}$			35					-44	100					
10 $u_{\text{O}_1\cdots\text{C}_1}$					-61	30				100				
11 $u_{\text{O}_1\cdots\text{C}_4}$							30				100			
12 $u_{\text{C}_1\cdots\text{C}_4}$												100		
13 $u_{\text{O}_1\cdots\text{C}_3}$							38		-22				100	
14 Scale								25		20				100

Table 3. Comparison of the ring angles and the bond distance C-O in 2,4,6-trimethyl-trioxan and in 1,3,5-trioxan.

		$r(\text{C-O}) \text{ \AA}$		$\angle \text{OCO}^\circ$		$\angle \text{COC}^\circ$	
2,4,6-Trimethyl-trioxan (this work)	Electron diff.	1.410	(0.004)	110.7	(0.7)	112.3	(0.8)
	X-Ray diff. ¹⁰	1.421	(0.006)	109.6	(0.3)	110.4	(0.3)
1,3,5-Trioxan	X-Ray diff. ¹¹	1.429	(0.004)	107.8	(0.2)	108.0	(0.2)
	Electron diff. ⁷	1.411	(0.002)	111.0	(0.7)	109.2	(1.0)
	Micro- wave ¹²	1.411	(0.01)	111.2	(1.0)	108.2	(1.0)
	Micro- wave ¹³	1.403	(0.002)	112.0	(0.3)	110.4	(0.3)

electron diffraction and microwave investigation of 1,3,5-trioxan the agreement between the results is very good, and in these investigations the $\angle \text{OCO}$ is found to be greater than the $\angle \text{COC}$. In the X-ray diffraction investigations of 1,3,5-trioxan and in this investigation of 2,4,6-trimethyl-trioxan, however, the $\angle \text{COC}$ is found to be greater. It is also seen from Table 3 that the ring angles are somewhat greater in 2,4,6-trimethyl-trioxan and consequently the ring is less puckered, as expected from the effect of the larger equatorial groups. A recent article⁹ on the structure of 1,3,5-trioxan suggests on the basis of potential energy calculations that the order of the two angles is in agreement with that found for 2,4,6-trimethyl-trioxan.

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