# The Molecular Structure of Dimethoxymethane, $CH_3—O—CH_2—O—CH_3$

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The molecular parameters and the conformation of dimethoxymethane (methylal) have been determined in the vapour phase by the electron diffraction method.

The structure investigation of dimethoxymethane has been carried out as part of a study on cyclic and acyclic ethers. The purpose of these investigations is to study the effect of ether oxygen atoms in chains and rings on the conformational arrangement.

Dimethoxymethane has previously been investigated by electron diffraction by Donohue [1] in 1950 and by Aoki [2] in 1953. Donohue, in his not published but quoted work, apparently assumed a planar all-*anti* conformation. Based on dipole moment measurements [3] 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 investigation was based on visually estimated intensity data.

The experimental data were collected at two nozzle-to-plate distances, 25 and 50 cm, using a Balzers electron diffraction unit. The data extend over the $s$-range 1.75 – 29.25 $Å^{-1}$. The electron wavelength was 0.0584 Å and the nozzle temperature approximately −18°C. The photographic plates were microphotometered. The molecular parameters have been refined by least squares method.[4] A diagonal weight matrix was employed throughout. A satisfactory fit to the observed intensity data was achieved using the parameters shown on Fig. 1. The experimental and the theoretical radial distribution curves are shown in Fig. 2.

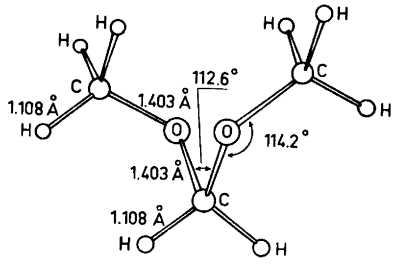


*Fig. 1.* Preliminary structure of dimethoxymethane. The C – O – C – O dihedral angle is 66.3°.

The angles HCH are so far assumed to be tetrahedral. The apparently unfavourable interaction of the lone pair electrons on the oxygen atoms in an all-*anti* conformation favours a *gauche gauche* conformation. The C – O – C – O dihedral angle is found to be 66.3°.

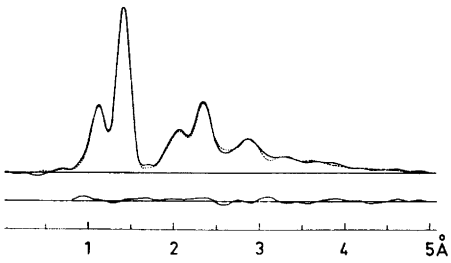


*Fig. 2.* Dimethoxymethane. Experimental (———) and theoretical (– – –) radial distribution functions. $k = 0.0015$ $Å^2$.

The dipole moment of dimethoxymethane in benzene, measured by Krane,[5] is found to be 0.99 D. Dipole moments of some related ethers given in the literature [6] 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 dipole moment of the determined structure of dimethoxymethane at this stage of refinement is calculated to be 1.2 D if each oxygen atom is assumed to have a moment of 1.2 D.

There is a possibility of two slightly different C – O bond distances in dimethoxymethane. This is indicated by the $u$-value of the average C – O bond distance (0.058 Å) which is found to be a little larger than usual.

The C – O bond distance is close to 0.02 Å shorter than determined by Aoki. The OCO and COC angles, assumed to be tetrahedral by Aoki, have been found to be larger and not equal in this work resulting in a more stretched chain.

The parameters of the thermal vibrations indicate a normal rigid molecule. The radial distribution curve does not seem to contain contributions from more than one conformation.

Further refinements of the structure are in progress.

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## The Content of *trans*-Aconitic Acid in *Asarum europaeum* L. Determined by Means of a Chromatogram Spectrophotometer

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In a previous investigation on the non-volatile acids of *Asarum europaeum* L. large amounts of *trans*-aconitic acid were detected.[1]

It has for long been known that the metabolic active form of aconitic acid is the *cis*-isomer, and this might account for the fact that this compound rarely cumulates in the tissue. In certain monocotyledons, like grasses and the sugar cane, *trans*-aconitic acid has been found in considerable amounts, for which reason Stout *et al.*[2] have coined the term "aconitate accumulators" for plants that contain more than 1 % of *trans*-aconitate on a dry weight basis.

The enzyme aconitase reacts specifically with the *cis*-isomer. This might result in the cumulation of the *trans*-isomer. In some plants, however, it has been observed that the *trans*-isomer is converted into the *cis*-isomer and thus brought into the TCA-cycle.[3]

*trans*-Aconitic acid has been reported to possess anti cancer effect *in vitro*,[4] and to inhibit respiration in the rat kidney cortex and in liver slices, which suggests the *trans*-isomer to be an aconitase competitor in the TCA-cycle.[5]

Based on the main constituents of the essential oil, Stahl and Jork [6,7] divided the species *Asarum europaeum* L. into four chemical races. It was found of interest to investigate if there existed corresponding differences in the *trans*-aconitate content of the four races, and to which extent the content of *trans*-aconitic acid in the different parts of the plant is influenced by the age, and by the state of development of the leaves. The investigation revealed that there are no remarkable differences in the *trans*-aconitic acid content in the four different races of the *Asarum europaeum* L., but the content of the acid is so high (up to 11 % dry weight) that the plant, according to Stout *et al.*[8] should be classified as an aconitate cumulator.

*Experimental.* Leaves, stems, and rhizomes of the plant were dried for 2 h at 70°C and pulverized. Dried and thoroughly mixed powder of the different samples, corresponding to 1 g of the fresh plant, was mixed with 1 ml of 25 % hydrochloric acid and 4 g of Silica gel (0.2 – 0.5 mm). The mixture was transferred to a glass column and extracted with 250 ml of acetone, whereupon the extract was evaporated to dryness *in vacuo*, and the residue dissolved in 25.00 ml of acetone. (1 ml of the solution corresponds to 40 mg of fresh plant.) 2 – 10 µl of the solution were applied on the thin-layer plates and chromatographed with 2 – 5 µg of pure *trans*-aconitic acid dissolved in acetone as a reference sample. The plates were coated with layers of cellulose Macherey Nagel MN 300. The thickness was increased to 500 µ, which caused a better reflection of the background. Pentanol-formic acid (98 %)-water (50:50:2.5) served as developing solvent. The plates were dried after the development for 1/2 h at 110°C. The acid appeared as a dark spot