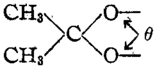
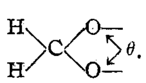
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Electric Moments of Dialkoxyalkanes

BY M. M. OTTO

Farmer and Wallis[1] measured the electric moments of some cyclic 1,1-dicarboxylic esters in order to test the valency deflection hypothesis of Ingold and Thorpe.[2] To explain the ease of formation of cyclic compounds from acetaldehyde and acetone with polyhydroxy compounds, Hill and Hibbert[3] used a modified postulate of Ingold and Thorpe, namely, that the valence angle of the carbon atom having two oxygen atoms attached to it was altered as the other two groups were varied. The angle θ in a compound containing the group  is less than the angle θ in a compound containing the group . Substances containing this type of group, namely, the dialkoxyalkanes, were available and therefore this hypothesis could be subjected to a physical test.

Preparation of Materials and Apparatus

The 2,2-dimethoxyheptane, 2,2-diethoxyheptane and 2,2-dipropoxyheptane were prepared from the appropriate acetylene and alcohol using boron trifluoride and mercuric oxide as a catalyst by G. F. Hennion.[4] Care was exercised to keep water and acid out of these compounds as they are very easily hydrolyzed. The compounds were fractionally distilled under reduced pressure through a good column. The boiling points, density and refractive index are listed in Table I. Diethoxymethane was purchased from the Eastman Kodak Co. and distilled; a fraction boiling at 87–88° was collected. Dineopentoxymethane[5] was formed as a by-product in the preparation of *t*-butylcarbinol. It can be distilled at atmospheric pressure without decomposition.

TABLE I

BOILING POINT, DENSITY AND REFRACTIVE INDEX OF DIALKOXYALKANES

Compound	B. p. °C.	Mm.	d^{25}	$n^{25}D$
2,2-Dimethoxyheptane	74–75	27	0.8451	1.41216
2,2-Diethoxyheptane	82–83	17	.8214	1.41656
2,2-Dipropoxyheptane	100–101	16	.8221	1.42697
Diethoxymethane	87–88	756	.8281	1.37095
Dineopentoxymethane	182–183	750	.8129	1.40494

The dielectric constants were determined using the apparatus previously described.[6] Density and refractive index were determined as in a previous article.[7]

Calculations

Hedestrand[8] obtained a formula for P_∞ which is listed below

$$P_\infty = A\left(M_2 - \beta\frac{M_1}{d_1}\right) + \beta\alpha$$

where

$$A = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \times \frac{1}{d_1} \qquad B = \frac{3M_1}{d_1(\epsilon_1 + 2)^2}$$

and ϵ_1, d_1, M_1 are the dielectric constant, density and molecular weight of the solvent and M_2 is the molecular weight of the solute. The values of α and β were obtained from the following equations for the dielectric constant and the density d of the solution: $\epsilon = \epsilon_1 + \alpha f_2$ and $d = d_1 + \beta f_2$.

If α and β are not functions of the concentration, then by rearrangement $\alpha = (\epsilon - \epsilon_1)/f_2$ and $\beta = (d - d_1)/f_2$, the value of either may be positive or negative. In the case of the compounds considered here there is a slight variation of α with concentration and little or no variation of β with concentration. To use the equation for P_∞ the value of α must be known where $f_2 = 0$. This could be obtained by plotting ϵ against f_2 and obtaining the tangent to the curve at $f_2 = 0$. It is much easier to plot α against f_2 and extrapolate to zero concentration.

To determine α it may be seen that the absolute value of the dielectric constant of the solution and solvent need not be known but only the difference between them or a constant times the difference, assuming, of course, that this constant may be determined. By the method used to determine the dielectric constant the capacity of the cell is measured, filled with the solution, in terms of scale divisions on a standard condenser or equivalent divisions read from a calibration chart, allowance being made for parasitic capacity. To find the dielectric constant the capacity of the cell is measured containing air and this value divided into the first capacity.

It is readily seen that the difference in scale reading between the solvent and the solute is a constant (*a*) times the difference between the di-

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(1) Farmer and Wallis, *J. Chem. Soc.*, 1304 (1933).

(2) Beesley, Ingold and Thorpe, *ibid.*, **107**, 1080 (1915).

(3) Hill and Hibbert, THIS JOURNAL, **45**, 3122 (1923).

(4) Hennion and Nieuwland, to be published, *cf. ibid.*, **56**, 1384 (1934).

(5) Conant, Webb and Mendum, *ibid.*, **51**, 1246 (1929).

(6) Otto and Wenzke, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 187 (1934).

(7) Otto and Wenzke, THIS JOURNAL, **56**, 1314 (1934).

(8) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

electric constants, the constant (a) being of course the capacity of the cell filled with air. If we plot αa against f_2 and extrapolate to zero concentration, a value is obtained which when divided by (a) gives α which may be used in the formula to determine (P_∞) polarization at infinite dilution.

This method of extrapolation tends to minimize errors, for the same absolute error in each case of plotting would mean a smaller percentage error in the method of plotting a constant times α than itself. As most of the data in the literature record the dielectric constant of the solution, these are tabulated for comparison and are listed in Table II together with the density.

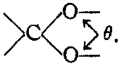
TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF DIALKOXYALKANES

(Solvent, Benzene; Temp., 25°)

c_2	d^{25}	ϵ
	2,2-Dimethoxyheptane	
0.03255	0.8695	2.2916
.04515	.8688	2.2975
.10480	.8652	2.3257
.12797	.8636	2.3361
	2,2-Diethoxyheptane	
0.03455	0.8675	2.2905
.04989	.8656	2.2974
.07161	.8630	2.3059
	2,2-Dipropoxyheptane	
0.03961	0.8670	2.2966
.06069	.8646	2.3062
.08211	.8625	2.3170
	Diethoxymethane	
0,05277	0.8693	2.3065
.07520	.8680	2.3199
.08952	.8671	2.3283
.10890	.8661	2.3392
	Dineopentoxymethane	
0.01684	0.8696	2.2802
.03896	.8662	2.2853
.06024	.8628	2.2906

Discussion of Results

As the angle between the two oxygen bonds in for example 2,2-dimethoxyheptane is not 180°, there must be the possibility of rotation about the C–O bonds which would alter the distance between the two methyl groups. This rotation cannot be spoken of as entirely free because of the small distance of the rotating groups from one another. There must also be a pronounced inductive effect of one bond upon another and therefore it may be concluded that the system is too complicated to obtain any quantitative measurement of the angle, *i. e.*,  It should be possible, however, to determine whether this angle varied, because this could be assumed to affect the measured moment.

This conclusion is substantiated by the fact that *o*, *m* and *p*-dimethoxybenzene have the moments 1.3, 1.58, 1.81 × 10^{-18}, respectively, while *o*, *m* and *p*-diethoxybenzenes have values 1.37, 1.70 and 1.76 × 10^{-18}, respectively,[9] where the angle between the line joining the oxygen to the ring carbon increased from 60 to 120 to 180°. In the compounds studied the doublets are much closer together but it is reasonable to assume that the effect for various valence angles (doublets in all cases still close together in comparison to above) is not different enough to compensate for any effect which might be due to the angle change.

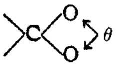
Table III indicates that within experimental error the moment of a compound having two hydrogen atoms attached to a carbon atom with two oxygen atoms is the same as those having an amyl group and a methyl group attached. This should be evidence that the different groups do not alter the angle in question although it is possible that there could be a balancing of several factors which would make the moment constant. A widening of the angle would tend to lower the moment but if at the same time the O–R doublets are further removed from each other and therefore free to rotate in positions of larger moment, the moment could remain constant. Not only must there be these effects but they must compensate each other. It is very much easier to assume the angle constant.

TABLE III

POLARIZATIONS AND ELECTRIC MOMENTS OF DIALKOXYALKANES

Compound	P_∞	MR_D	$\mu \times 10^{18}$
2,2-Dimethoxyheptane	63.83	47.17	0.90
2,2-Diethoxyheptane	74.29	57.56	.90
2,2-Dipropoxyheptane	84.98	67.52	.92
Diethoxymethane	46.23	28.49	.92
Dineopentoxymethane	72.84	56.73	.88

Summary

1. Evidence is offered for the constancy of the valence angle of  where the two other attached groups are two hydrogen atoms and that

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(9) Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929).

containing an amyl group and a methyl group.

2. Electric moments have been determined for 2,2-dimethoxyheptane, 2,2-diethoxyheptane, 2,2-dipropoxyheptane, diethoxymethane and dineopentoxymethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Action of Molten Lithium Salts on Glass[1]

BY OLUS J. STEWART AND DAVID W. YOUNG

Burt[2] in describing his attempt to pass lithium ions electrolytically through the wall of a sodium coulometer by operating the instrument in a bath of molten lithium nitrate, wrote: "If the nitrate of lithium, a smaller ion than sodium, is used in place of sodium nitrate, the glass of the bulb in a few minutes closely resembles a white eggshell; it is very weak and will not hold a vacuum."

While repeating Burt's experiment the senior author of this paper shortly observed that a thermometer bulb which dipped into the bath of molten lithium nitrate had dropped off, a second thermometer soon failed to function and a stirring rod, subsequently introduced, quickly turned white. Examination showed that the surface of the immersed glass was covered with a network of nearly microscopic fractures which gave it an etched appearance. This phenomenon differed from that observed by Burt. The former was non-electrolytic, the latter electrolytic. Investigation shows that the phenomenon is a manifestation of a metathetical reaction wherein lithium ions replace sodium ions in glass and the decrease in weight of the glass is a measure of the lithium involved. The superficial fracturing of soda-lime glass in the manner indicated appears to be a phenomenon uniquely effected by molten anhydrous lithium salts and provides a simple means for identifying the element. The reaction is not limited to the surface of the glass but may penetrate the interior.

The Identification of Lithium.—On cautiously and repeatedly passing through a flame a common soda-lime test-tube, rod or microscope slide to which adheres a drop of lithium nitrate solution, the water will evaporate and the anhydrous salt will melt. After slight additional heating, followed by the cooling, washing and drying of the glass, it will be observed that that portion of the glass which has been in contact with a sufficient quantity of melted lithium nitrate is white. Suitable illumination then will show the whitening of the glass is due to a multitude of fractures which are visible to the naked eye, but are more readily observed under a magnifying glass.[3]

If the drop of solution under examination contains as much as 0.00005 g. of lithium, the fractures will be so numerous that the glass will be white or etched, but when working with very dilute solutions careful examination of the glass under a microscope is required to discover the few scattered fractures. The smallest quantity of lithium we have been able to detect in a drop of solution by this micro method is 1×10^{-6} g. which, assuming 20 drops to the ml., represents 0.00002 g. of lithium per ml. The test for lithium may be carried out in the presence of the salts of other elements, but the latter may reduce the effectiveness of the former by dilution, by formation of mixed crystals and by etching or roughening the glass surface. Pyrex glass is not fractured by lithium.

The Estimation of Lithium.—A quantity of standard lithium nitrate solution from a weight buret was evaporated to dryness in a small weighed Pyrex beaker provided with a stirrer. After adding a known quantity of coarsely ground glass wool, sufficient water (2–4 ml.) was introduced to redissolve the salt and permit thorough mixing. Prompt evaporation to dryness was followed by heating for a period of one to two hours at approximately 310°. When the beaker had cooled, water (2–4 ml.) was added for dissolving the sodium nitrate produced in the re-

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(1) A portion of this communication formed the basis of a thesis submitted by David W. Young in partial fulfilment of the requirements for the degree of Master of Science at the University of Kentucky, 1935.

(2) Burt, *J. Opt. Soc. Am.*, **11, 87 (1925).**

(3) The analysis of the Automatic Machine Made test-tubes used in this part of the work was kindly furnished by Kimble Glass Company, Vineland, N. J.: SiO_2 67.7, $Al_2O_3(Fe_2O_3, TiO_2)$ 2.8, CaO 5.5, MgO 3.9, BaO 2.0, Na_2O 14.8, K_2O 1.3, B_2O_3 1.3, Sb_2O_3 0.2, ignition loss 0.2.