[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY][1]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. XLVII. The Oxygen Valence Angle and the Structure of Glucose and Related Compounds[2]

BY J. STANLEY ALLEN AND HAROLD HIBBERT

Introduction

In preliminary communications[3] the relationship existing between the electric moment of certain molecules containing an oxygen atom and the oxygen valence angle was discussed. Since this article was first submitted, a paper by Smyth and Walls[4] has appeared in which they conclude that the oxygen valence angle in the diphenyl ethers is 121 ± 5°. They also find that the oxygen valence angles in various heterocyclic compounds vary from 65 to 140° and that the moments found experimentally are in excellent qualitative agreement with predictions based on the size of these angles. In this paper, an attempt is made to determine the magnitude of the oxygen valence angle in a series of simple heterocyclic compounds as well as in an additional complex molecule, by recognized methods of mathematical analysis of the electric moment as used elsewhere by many others.[5]

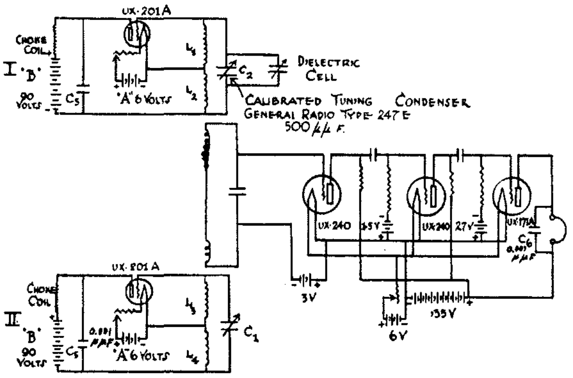


Fig. 1.—Improved heterodyne beat apparatus for measurement of the dielectric constant of liquids.

Apparatus

The apparatus used for measurement of the dielectric constant was similar to that employed by Williams and by Smyth.[6] A complete diagram of the apparatus is given (see Fig. 1). The vernier knob of the tuning condenser, C_2, was replaced by a small brass pulley, this being connected by a stout cord to a set of large wooden pulleys, so that the observer was sufficiently far removed to avoid body capacity effects. This arrangement gave an accuracy in capacity readings of 0.02 μμf. The two oscillators and amplifier were shielded in separate galvanized iron boxes, which were grounded, and the connecting wires used in coupling passed through small holes, since it is known that the decrease in shielding efficiency is less with a small hole than with a slit of the same area.[7] The dielectric cell employed was similar to that used by Williams and Krchma.[8] The condenser consisted of five "stator" and four "rotor" plates of gold-plated brass. The brass "rotor" axle passed through two supports, one of brass, soldered to the stator plate extensions, 2.5 or 5 cm. above the plates. The axle was insulated from the support by a piece of snugly-fitting glass tubing and the tube was held rigidly in place by a small wedge of copper. The use of bakelite insulation, objected to by Smyth, was thus avoided. The other bearing, also of brass, was bolted to the insulating frame.

Two determinations of the dielectric constant of benzene gave $\epsilon = 2.275$ and $\epsilon = 2.278$, each value being in good agreement with previous determinations.[4,6a,9] The value $\epsilon = 2.276$ was used throughout.

All measurements were made at 25 ± 0.05° at a frequency of about 10^6 cycles per second.

Refractive indices of the pure liquids were measured at 25° with an Abbé refractometer and the calculated values of the molar refraction obtained by using the following values for the atomic refraction: carbon singly bound, 2.501; hydrogen, 1.065; oxygen (hydroxyl) 1.521, oxygen (ether) 1.683, oxygen (ketonic) 2.287; chlorine, 5.967; 3-ring, +0.71;[10] 4-ring, +0.48.[10]

The density bottle was similar to that used by Isnardi[11] and described by Smyth and Morgan.[12] It was standardized with pure water and benzene. The density of pure benzene determined from several measurements was d_4^{25} 0.8734 ± 0.0002.

Preparation of Materials

I. Preparation of Glycol Monochloroacetate.—Monosodium glycolate was prepared by heating sodium methylate (obtained from 11.5 g. of sodium) and ethylene glycol

---

[1] With financial assistance from the National Research Council of Canada and the Canadian Pulp and Paper Association.

[2] From Part II of a thesis presented by J. Stanley Allen in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, McGill University.

[3] (a) Allen and Hibbert, *Ber.*, **65**, 1362 (1932); (b) Hibbert and Allen, THIS JOURNAL, **54**, 4115 (1932).

[4] Smyth and Walls, *ibid.*, **54**, 3230 (1932).

[5] (a) Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929); (b) Hojendahl, *Nature*, **117**, 892 (1926); (c) Smyth and Morgan, THIS JOURNAL, **49**, 1030 (1927); (d) Smyth and Walls, *ibid.*, **54**, 1854 (1932); (e) Thomson, *Phil. Mag.*, [6] **46**, 497 (1923); (f) Williams, *Chem. Reviews*, **6**, 549 (1929).

[6] (a) Williams, THIS JOURNAL, **52**, 1831 (1930); (b) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., N. Y., 1931.

[7] Lyons, unpublished data in personal communication.

[8] Williams and Krchma, THIS JOURNAL, **48**, 1888 (1926).

[9] (a) Ball, *J. Chem. Soc.*, 570 (1930); (b) Hartshorn and Oliver, *Proc. Roy. Soc.* (London), **A123**, 664 (1929).

[10] Oestling, *J. Chem. Soc.*, **101**, 457 (1912).

[11] Isnardi, *Z. Physik*, **9**, 153 (1922).

[12] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

(47 g.) in a nitrogen atmosphere; 60 cc. of methyl alcohol was recovered.

After cooling, 65 g. of chloroacetyl chloride (in 125 cc. of ether) was added slowly, the mixture being kept at 10°. On allowing the temperature to rise to 20°, evolution of heat occurred, and some ether distilled over. The liquid was decanted from the salt residue and the ether removed at as low a temperature as possible. The residual yellowish liquid was poured into water and the upper aqueous layer (A), containing the monochloroacetate, retained. Glycol bis-monochloroacetate is insoluble. The monochloroacetate solution (A) was saturated with common salt, the solution extracted with ether, dried with alumina, and the ether removed; crude yield, 79%. Careful fractionation under reduced pressure yielded 18 g. of glycol monochloroacetate (25%) b. p. 87–90° (0.60 mm.), which on final redistillation gave 8.1 g. of b. p. 85° (0.15 mm.). (bath temperature 110°). This and the following products were kept in a desiccator over anhydrous calcium chloride prior to use.

Glycol monochloroacetate was also prepared from ethylene oxide and chloroacetic acid, in smaller yield, but free from by-products, according to the following procedure.

Redistilled monochloroacetic acid was dissolved in pure anhydrous ether and to the mixture in a pressure bottle ethylene oxide (50% excess) was added at 0°, and the mixture allowed to stand four days at this temperature. The ether was removed at a low temperature, the residue poured into a small amount of water and the glycol monochloroacetate salted out with sodium chloride. The solution was extracted with ether, the ether solution washed with sodium bicarbonate, dried and the ether removed. Repeated vacuum distillation gave a pure product, b. p. 83° (0.08 mm.); 240° (760 mm.) (with decomposition), n^{25}_{D} 1.4585.

II. **Preparation of Glycol Monodichloroacetate (2-Hydroxy-2′-dichloromethyl-1,3-dioxolane).**—Pure redistilled dichloroacetic acid (50 g.) dissolved in about 50 cc. of anhydrous ether was mixed in a pressure bottle with 30 g. (50% excess) of pure dry ethylene oxide at 0° and allowed to stand for fifty-six hours at 0°. The mixture was washed with 50 cc. of water, the ether layer separated and then washed with saturated sodium bicarbonate solution until neutral, again with water, dried, and the ether removed below 40°. Repeated vacuum fractionation gave a colorless liquid, insoluble in water, b. p. 106° (0.08 mm.) (bath temperature 125°), n^{25}_{D} 1.4730; yield 10 g.

III. **Preparation of Trimethylene Oxide.**—Trimethylene oxide was prepared by the action of solid potassium hydroxide on γ-bromopropyl acetate,[13] the latter being obtained by a modification of a similar method used by Bogert and Slocum.[14]

(a) **γ-Bromopropyl Acetate.**—Trimethylene glycol (85 g.) was purified by redistilling twice under reduced pressure, yielding a product with only a faint color, and then acetyl bromide (250 g.) distilled, very slowly, into the glycol at 0°. The mixture was allowed to stand for twenty-four hours, and then heated on a water-bath for two hours, until evolution of hydrogen bromide ceased. Carbon tetrachloride (300 cc.) was added and the mixture distilled slowly at a temperature of 72–85°. The distillate, consisting of water and carbon tetrachloride, was neutralized with sodium carbonate each time 100 cc. had collected, and the carbon tetrachloride returned through a dropping funnel at the same rate at which the distillate condensed. The process was continued until no water appeared in the distillate, at which time about 500 cc. of carbon tetrachloride had been distilled. The mixture was heated to 120°, cooled, and washed twice with water to remove trimethylene bromohydrin. The lower layer, after separation, was neutralized with sodium carbonate and dried with alumina. Final fractionation using a Claisen flask gave 154 g. (78% yield) of b. p. 81–86° (20 mm.), bath temperature, 100°.

When this preparation was well advanced, a simpler method[15] became available, and this suggested some of the modifications indicated above.

(b) **Trimethylene Oxide.**—A round copper flask (500 cc. capacity) was connected to an air condenser 120 cm. high by a well-fitting ground-glass joint. The air condenser was fitted with a Claisen type fractionation column, which in turn was connected to a water condenser and a condenser coil placed in an ice–salt mixture; potassium hydroxide (240 g.) and water (10 cc.) were placed in the copper flask. This mixture fused at 150° and was kept at that temperature by an oil-bath heated to 170°. γ-Bromopropyl acetate (148 g.) was added slowly drop by drop. White fumes were formed and distillation of trimethylene oxide took place at the rate of a drop per second. As addition of the acetate continued the bath temperature was raised 10° every half hour to 200°. The crude distillate was dried with anhydrous potassium carbonate and redistilled. Slow fractionation in a Claisen flask gave 11 g., b. p. 45–50°, yield 21%. This fraction was treated with liquid bromine at 10°. A violent reaction took place and the bromine addition was continued until the color showed an excess was present. The reaction product was then dried with anhydrous potassium carbonate and redistilled. The distillate, which still contained unsaturated products, was again treated with a further quantity of bromine at −10°, this time a considerable excess being added. The reaction product was dried over solid potash and on careful repeated fractionation gave 2 g. of pure trimethylene oxide, b. p. 47.5–47.9°, n^{25}_{D} 1.3895 ± 0.0002, d^{25}_{4} 0.8930,[16] bath temperature 65°.

The only impurity of low boiling point in the crude trimethylene oxide was allyl bromide, which on bromination forms tribromohydrin (b. p. 222°). The difference in boiling point between this compound and trimethylene oxide permits of a ready separation of the latter in a pure state.

IV. **Purification of Propene Oxide (Propylene Oxide).**—Propylene oxide obtained from the Carbide and Carbon Chemicals Corporation was dried with alumina. It was twice fractionally distilled, b. p. 34.75–34.90°; d^{25}_{4} 0.8249 ± 0.0002.

V. **Preparation of Tetrahydropyran (Pentamethylene Oxide).**—Pentamethylene dibromide was very carefully

---

[13] Noller, unpublished data in private communication.

[14] Bogert and Slocum, This Journal, **46**, 763 (1924).

[15] Clarke and Rahrs, unpublished data in private communication.

[16] Derick and Bissell, This Journal, **38**, 2478 (1916).

fractionated through a column of glass beads contained in the side arm of a Claisen flask. After three distillations, a fraction of b. p. 93.5° (9 mm.) was obtained. An attempt to prepare the tetrahydropyran by Dem'yanov's[17] method yielded mostly unchanged dibromide. The oxide was obtained as follows:

A mixture of 25 g. of pure dibromide, 25 g. of distilled water and 8 g. of pure zinc oxide was sealed in a strong hard-glass tube, shaken to an emulsion and then heated in a bomb furnace for forty hours at 150°. The reaction mixture was extracted three times with ether, the extract dried over sodium sulfate, and fractionated. The united fractions, b. p. 85–90°, from three preparations, gave on further careful fractionation a pure product; b. p. 87.5–88.5°, d_4^{25} 0.8772, n_D^{21} 1.4211, n_D^{25} 1.4195, yield 90%.

Experimental Part

The electric moments of molecules of several compounds have been determined by the use of suitable binary mixtures, by a method described previously.[5c,18]

Table I contains the experimental results used to determine the electric moments. The first column, f_2, gives the mole fraction (in per cent.) of the polar substance in benzene solution, and succeeding columns give the dielectric constant, ϵ, and density, d, at 25°, the polarization $P_{1,2}$ of the mixture and the total polarization, P_2, of the polar solute. The moments of the true glycol half-esters are about 0.1×10^{-18} e. s. u. too high due to neglect of the atomic polarization.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

f_2, %	ϵ	d_4^{25}	$P_{1,2}$ cc.	P_2, cc.
Propylene Oxide				
0.0000	2.276	0.8734	(26.68 = P_1 of benzene)	
.5593	2.303	.8732	27.02	88.2
.8191	2.315	.8731	27.18	88.4
2.1318	2.373	.8725	27.94	85.6
2.5055	2.383	.8724	28.04	80.0
5.7758	2.519	.8711	29.67	78.5
Trimethylene Oxide				
0.0000	2.2760	0.8734	(26.68 = P_1)	
.3072	2.2945	.8734	26.91	100.9
.3759	2.2970	.8734	26.94	97.3
.8023	2.3194	.8735	27.27	96.0
Tetrahydropyran (Pentamethylene oxide)				
0.0000	2.276	0.8734	(26.68 = P_1)	
.3788	2.294	.8735	26.94	95.2
.6560	2.306	.8736	27.11	92.7
2.0463	2.355	.8739	27.85	83.6
3.1684	2.406	.8742	28.59	86.9
3.1776	2.407	.8742	28.61	87.0
Glycol Monochloroacetate				
0.0000	2.275	0.8733	(26.66 = P_1)	
.0873	2.334	.8746	27.53	330.6
.4501	2.359	.8753	27.90	306.7
.8233	2.420	.8772	28.76	283.1
.9220	2.432	.8776	28.94	280.9
1.0581	2.449	.8785	29.17	264.5
Glycol Dichloroacetate (Ring)				
0.0000	2.275	0.8733	(26.66 = P_1)	
.1701	2.300	.8741	27.05	261.3
.2089	2.306	.8747	27.14	250.7
.2163	2.306	.8745	27.14	251.4
.2610	2.315	.8754	27.26	259.3
.3484	2.322	.8756	27.38	234.1
.3658	2.330	.8758	27.49	256.2
.5019	2.347	.8768	27.75	245.1
.6818	2.373	.8782	28.14	244.2
.7899	2.389	.8790	28.36	243.7
1.0020	2.443	.8807	29.13	274.0

The first column of Table II gives the compound, and the polarization, P_∞, at infinite dilution ($f_2 = 0$), the molar refraction ($MR_D = P_E$), the orientation polarization ($P_\infty - MR_D = P_M$), and the electric moment ($\mu \times 10^{18}$) follow in order. The absolute values of the moments are a little high because of the neglect of the atomic polarization P_A.

TABLE II

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	P_∞, cc.	P_E, cc.	P_M, cc.	$\mu \times 10^{18}$, e. s. u.
Ethylene oxide	...	...	...	1.88[6b]
Propylene oxide	90.1	16.29	73.8	1.88
Trimethylene oxide	100	16.06	84	2.01
Tetrahydrofuran	80.7	19.76	60.9	1.71[4]
Tetrahydropyran	96.0	22.84	73.1	1.87
Glycol monochloroacetate	352.0	28.92	323.1	3.94
Glycol dichloroacetate (ring)	266.6	33.21	233.4	3.35

The oxygen valence angles have been calculated for the cyclic ethers, the values of which are

TABLE III

OXYGEN VALENCE ANGLES OF CYCLIC ETHERS

Compound	Moment ($\times 10^{18}$)	Oxygen valence angle
Ethylene oxide	1.88	70°[a], 65°[4]
Propylene oxide	1.88	70°
Trimethylene oxide	2.01	94°
Tetrahydrofuran	1.71[4]	108°, *ca.* 100°[4]
Tetrahydropyran	1.87	93°
Glycol dichloroacetate (1-hydroxy-1'-dichloromethyl-1,3-dioxolane)	3.35	*ca.* 90°

[a] These angular values differ from those previously reported (3b) due to the application of a value of the C–O internuclear distance obtained subsequently by Brú.[20]

---

(17) Dem'yanov, *J. Russ. Phys.-Chem. Soc.*, **45**, 169 (1913); *C. A.*, **7**, 2226 (1913).

(18) (a) Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927); (b) Williams and Weissberger, *ibid.*, **50**, 2332 (1928).

included with that of the dioxolane ring compound in Table III.

Discussion of Results

It has been evident for some time that, in the interpretation of the electric moment data for water, alcohols, ethers, etc., some stereochemical effect of the oxygen atom had to be taken into account in correlating these data with the structure of the individual molecules. Previous calculations of the electric moments of oxygen compounds from the equations of vector addition have been based on the assumption, without proof, of the tetrahedral nature of the oxygen atom.

Smyth and Walls[4] have calculated the value of the oxygen valence angle in ethylene oxide as 65°, on the assumption that the interatomic distances are unchanged in the triangular molecule. They used values for the internuclear distances of C–C = 1.54 Å. and C–O = 1.43 Å.[19] A previous incorrect calculation, made by us, assuming C–O = 1.18 Å.[3a] showed the same oxygen valence angle to be about 80°. Brú[20] has since measured the carbon–oxygen internuclear distance in methyl and ethyl ethers, and obtained the value C–O = 1.34 ± 0.06 Å. It would seem that the theoretical value of the C–O separation suggested by Pauling is too large, so that the only experimental value, that obtained by Brú, is used in preference.

In the cyclic compounds studied, the molecules may have more closely defined geometrical structures than are to be expected in open-chain compounds. In the ethylene oxide molecule the structure is comparatively rigid, and the valence angles have quite definite values, which are defined if the C–C and C–O internuclear separations are known and constant. If the experimental values given above are used, the oxygen valence angle in ethylene oxide is 70°, and the carbon angles are 55°. This gives the value of the group moment $m(\mathrm{CH_3{-}O}) = 1.15 \times 10^{-18}$ e. s. u. The value of $\Theta = 70°$ for the oxygen valence angle is the *minimum for any C–O–C linkage.*

Preliminary calculations of the electric moments of certain molecules showed the oxygen valence angle to be about 90°. In view of the remarkable implications involved in this result, the electric moment of tetrahydropyran was measured ($\mu = 1.87$) and the moment calculated assuming $m(\mathrm{CH_3{-}O}) = 1.15$. The value of the bond moment m(H–C) is small, but not negligible, as will be shown later. Values of the Kerr constant[21] show that this bond moment has a finite value. It is usually assigned the value m(H–C) = 0.4.

That the six-membered tetrahydropyran ring is diplanar is undoubtedly true. If so, this "puckering" will enable the valence bonds to assume any convenient angle and thus any strain on these bonds will be very small. Hence the oxygen valence angle formed in tetrahydropyran may be practically strainless, and is therefore the "normal" angle, for this compound at least. Using the bond moment values above, assuming the oxygen valence angle $\Theta = 93°$, the calculated electric moment is 1.87, which would seem to confirm the value of $\Theta = 93°$. If Θ be 110°, the calculated moment is only 1.65. If, as has been suggested, the bond moment m(H–C) is less than 0.4 (let us say 0.2), then the calculated moment is 1.75 if $\Theta = 93°$, and 1.43 if $\Theta = 110°$. Regardless of the exact value of m(H–C), the only calculated values of the moment in agreement with experiment are based on the assumption $\Theta = 93°$, which result provides strong support for the view that the oxygen valence angle in tetrahydropyran is about 90°.

It will be noted that if m(H–C) is less than 0.4, the values of the oxygen valence angle must be *less* than 93° to be consistent with experimental results. This result provides good support for the first experimental confirmation by electric moment measurements of the value of 90° assigned to the oxygen valence angle by Pauling from quantum mechanical considerations.

The electric moments of propylene oxide and ethylene oxide are identical, as might have been reasonably predicted. This result confirms the conclusion that the moments of adjacent members of certain homologous series are identical. The oxygen valence angles of these oxides are also the same, about 70°. Since the triangular structure for ethylene oxide sets a minimum value for the oxygen valence angle regardless of its numerical value, it is impossible for any electric moment of a cyclic ether to be greater than that of ethylene oxide, unless other factors contributing to the moment are assumed. In the probable absence of measurable induction effects, this necessitates the conclusion that the H–C bond moments must contribute something to the electric moment.

---

[19] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

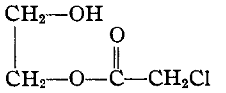
[20] Brú, *Anales soc. españ. fís. quím.*, **30**, 483 (1932); *C. A.*, **27**, 1269 (1932).

[21] Wolf, *Z. physik. Chem.*, **3B**, 128 (1929).

For trimethylene oxide, using $m(\mathrm{H{-}C}) = 0.4$, this contribution is 0.46 for the two H–C bonds opposite the oxygen atom. Since $\mu = 2.01$, this still leaves a contribution of 1.55 for the two $\mathrm{—CH_2{-}O}$ linkages.

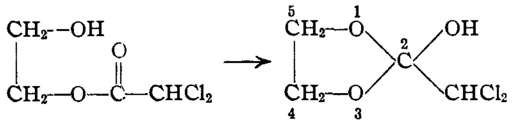
The electric moment of trimethylene oxide would almost appear to be too high. The only likely impurity was allyl bromide, which has a smaller moment than trimethylene oxide. In the measurement of $P_{1,2}$ (Table I) the low concentrations employed may cause an error of about 3 cc. in P_M, which would lower the moment to 1.97. In the four-membered trimethylene oxide ring we expect bond angles of about 90° for oxygen as well as carbon. The oxygen angle would be somewhat greater than 90°, since the C–O is less than the C–C distance. Calculation of this value from the moments leads to 94°, in satisfactory agreement.

There is considerable difference (0.59) between the moments of the two acetates (I and II).



$$\mathrm{CH_2{-}OH}\,|\,\mathrm{CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2Cl}$$

(I)



(II)

Hibbert and Greig[22] have shown that the isomer of glycol trichloroacetate is a dioxolane ring compound, and Meerwein and Sonke[23] have confirmed this fact. Furthermore, the isomer of glycol dichloroacetate also has the dioxolane structure and although the method of preparation would lead one to expect the open chain product, apparently only the ring isomer was obtained. (I) has been shown to be a normal half-ester, an open chain compound.[24] The relative values of the electric moments of these two compounds confirm the structural evidence already obtained.

The compounds (I) and (II) may be looked upon as derivatives of ethyl chloride and 1,1′-dichloroethane, respectively, since each contains two carbon atoms adjacent to the chlorine atoms. The electric moments of the chlorides are $\mu_{\mathrm{C_2H_5Cl}} = 1.99$ and $\mu_{\mathrm{C_2H_4Cl_2}} = 2.01$, indicating that the substitution by a chlorine atom in ethyl chloride produces no measurable inductive effect on the resultant moment. Thus in the electric moments of the above two compounds no observed difference is to be expected if they are both normal open-chain half-esters. Thus the total difference of 0.59 must be accounted for on the basis of other than constitutive factors. This could be best explained by ring closure, assuming a value of about 90° for Θ. The calculated value of the moment is 3.45. If $\Theta = 110°$, the moment is less than 3.0.

The theory that the normal oxygen valence angle is 90° rather than 109°28′ has been applied to numerous oxygen compounds, and certain discrepancies in behavior based on the tetrahedral theory have disappeared as a result. The most important of these is the fact that a pyranose ring is more stable than a furanose ring in carbohydrates and polysaccharides. For furanose derivatives the theory shows that this ring is planar and strained. Since the internuclear distances are C–C = 1.54 Å. and C–O = 1.34 Å., and the oxygen valence angle is less than the tetrahedral angle, it is evident that these two factors both contribute to the consequent instability of the ring.

A consideration of the same factors for the pyranose ring shows that this ring is a diplanar and hence strainless structure. This result is in complete agreement with the conclusions of Haworth[25] based on physical and chemical data, of Cox[26] from x-ray investigations and many others. The possible exception noted by Linnell and Melhuish[27] in their study of aceto-propyl and -butyl alcohols is not fully proved.

The theory explains why the polymethylene diols of Franke[28] on dehydration form 1,5-oxido compounds rather than the 1,4-oxido compound which would be expected on the assumptions of classical stereochemistry.

The formation of the dioxolane ring and the confirmation of the proof of the ring structure assigned to it by Hibbert and Greig[22] show that the compound is quite stable. An explanation of the stability of the dioxolane ring formed in the de-acetylation of the methyl acetyl-rhamnosides and mannosides observed by Haworth[29] and Freudenberg[30] is thus offered. By analogy, this

---

(22) Hibbert and Greig, *Can. J. Research*, **4**, 254 (1931).

(23) Meerwein and Sonke, *Ber.*, **64B**, 2375 (1931).

(24) Greig, Thesis, McGill University, 1932.

(25) Haworth, "Constitution of Sugars," Edward Arnold Co., London, 1929, Chaps. 4 and 5.

(26) Cox, *J. Chem. Soc.*, 2313 (1931); 133 (1932).

(27) Linnell and Melhuish, *Quart. J. Pharm. Pharmacol.*, **3**, 40 (1930).

(28) (a) Franke and Gomolka, *Monatsh.*, **53** and **54**, 577 (1929); (b) Franke and Kroupa, *ibid.*, **56**, 331 (1930); (c) Franke, Kroupa and Panzer, *ibid.*, **60**, 106 (1932).

(29) Haworth, Hirst and Miller, *J. Chem. Soc.*, 2469 (1929).

(30) Freudenberg, *Naturwiss.*, **18**, 393 (1930).

dioxolane ring is supposed to be a typical form of all such rings which are postulated as intermediates in certain well-known molecular rearrangements and group migrations, and explains the facility with which these transitions occur.[22]

The relative stability of γ- and δ-lactones would appear to be definitely an exception to this rule. There is some evidence that the carbon valence angle in the carbonyl group of ketones is about 132°. If this be so, then the greater stability of γ-lactones finds a satisfactory explanation, since the increased magnitude of the carbon valence angle cancels the effect of the decrease in the oxygen angle to about 90°. This suggestion, however, does not explain the relative instability of δ-lactones any more than the Sachse–Mohr theory. A possible explanation has been offered by Carothers[31] in connection with the remarkable tendency toward polymerization shown by certain six-membered cyclic esters.

It would appear that many of the properties of the oxide rings of carbohydrates and polysaccharides with respect to stability, ease of formation, and interconvertibility, can be explained on the basis that the oxygen valence angle is about 90°.

Acknowledgment.—We take this opportunity to acknowledge the kindness of Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company for the gift of the pentamethylene bromide and to thank Dr. Walter Mitchell of this Department for the preparation of the tetrahydropyran.

Summary

1. Trimethylene oxide and tetrahydropyran have been prepared, their densities and the dielectric constants of their dilute solutions, and those of propylene oxide measured. The electric moments are 2.01, 1.87 and 1.88 × 10^{18} e. s. u., respectively.

2. The "normal" oxygen valence angle has been determined for tetrahydropyran as 90 ± 5°. The "normal" angle is defined as that assumed by the valence bonds under ideal *intramolecular* conditions.

3. The value of the moment of propylene oxide supports the conclusions that substitution of a hydrogen atom by a methyl group causes no change in moment in certain homologous series. The values of the oxygen valence angle in some heterocyclic rings have been calculated and tabulated.

4. The electric moments of the monochloroacetate I and the cyclic form of the dichloroacetate (2-hydroxy-2-dichloromethyl-1,3-dioxolane) II are 3.94 and 3.35 × 10^{-18} e. s. u., respectively. The difference in the moments is explained by the formation of the dioxolane ring structure.

MONTREAL, CANADA RECEIVED APRIL 6, 1934

---

[31] Carothers, *Chem. Reviews*, **8**, 406 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Saponins and Sapogenins. I. Echinocystic Acid

BY I. BERGSTEINSSON AND C. R. NOLLER

Several species of plants belonging to the gourd family and native to the Pacific Coast are commonly called big-root, man-root, man-in-the-ground, wild cucumber or Chilicothe vine. Jepson[1] states that *Echinocystis marah* (*Megarrhiza marah*) is to be found in the hills of Marin, Alameda and Contra Costa counties and northward, *E. fabacea* (*M. californica*), the most common species, in the Coast Ranges and the Sacramento and San Joaquin valleys, *E. watsonii* in the Sierra Nevada and *E. macrocarpa* from the Kaweah River basin to Southern California.

As the common names imply, all of these species are especially characterized by a huge root weighing up to perhaps fifty kilos which can be readily imagined to resemble the body of a man. The portion above ground is a rather graceful vine which bears green round, or oval fruit with soft spines. It is likely that the roots of all species have been used as fish-poisons by the California Indians. Thus Chestnut[2] states that the Indians of Mendocino County used the root of *Magarrhiza marah* for this purpose and as a medicine. Extracts of one of the species, prob-

---

[1] W. L. Jepson, "Flora of Western Middle California," Cunningham, Curtiss and Welch, San Francisco, 1911, 2d ed., p. 270.

[2] Chestnut, "Contributions from the U. S. National Herbarium," **7**, 390 (1902).