

DIPOLE MOMENTS OF TETRAHYDROPYRAN AND DIHYDROPYRAN*

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INTRODUCTION

THE dipole moments of heterocyclic compounds are of interest both for an indication of the valency angle of the hetero atom and for information as to the spatial disposition of the members of a ring system. Pyrans have the added interest on account of their relationship with the hexoses. Since Allen and Hibbert¹ reported a value of 1.87 D for the dipole moment of tetrahydropyran, there have been improvements in the design of apparatus used as well as in experimental technique, especially in the design of constant frequency oscillators.^{7, 9, 15, 28} Besides, greater accuracy is also possible now in the extrapolation methods for computing τP_{∞} at infinite dilution.^{16, 17, 20, 23} It was therefore considered desirable to redetermine the value for tetrahydropyran. The results of measurements on tetrahydropyran and dihydropyran have been recorded here and their structures discussed in the light of the results obtained.

EXPERIMENTAL

Materials.—'AnalaR' benzene was repeatedly shaken with concentrated sulphuric acid, washed thoroughly with water, treated with a solution of sodium hydroxide, washed again with water and dried over anhydrous calcium chloride. The middle portion obtained by fractional distillation was frozen out. The portion freezing last was rejected and the benzene after melting was stored over pure sodium wire which retained its metallic lustre.

Tetrahydropyran obtained from the I.C.I. was dried over anhydrous sodium sulphate, distilled in an all-glass apparatus and the middle fraction collecting between 87° and 88° was used.

Dihydropyran obtained from the I.C.I. was dried over potassium hydroxide, distilled in an all-glass apparatus and the middle fraction collecting between 86° and 87° was used for the determinations.

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Apparatus.—Dielectric constant measurements were made with an A.C. mains operated heterodyne beat apparatus similar to that of Hudson and Hobbs²¹ with the following modifications. The crystal oscillator employed a hermetically sealed quartz crystal with a frequency of 1,000 kc./sec. and a temperature coefficient of 0.0001% per° C. and an RCA 6V6 valve, operated with a plate voltage of 250 V. The electron coupled critical oscillator with the radio frequency mixer was similar to that of Hudson and Hobbs. Following the radio frequency mixer, a three stage valve amplifier, specially suited to the operation of a pair of low frequency phones was used. An efficient electronic stabiliser circuit⁸ following the power supply was used to achieve complete stabilisation of plate potentials. To ensure frequency stability, the whole assembly was enclosed in an aluminium case and was maintained at a constant temperature of 35° C. by means of an air thermostat. Special attention was given to the rigidity of the mountings and shielded cables were used in all R.F. current carrying sections. Radio frequency chokes were employed in the L.T. lines to prevent stray R.F. currents. In the tank circuit of the crystal oscillator, in parallel with a variable air condenser of 0.0005 mfd was a coil of 50 turns of D.S.C. wire No. 20 S.W.G. wound on a bakelite former of 3" diameter with a length to diameter ratio of 1:1.37 because this ratio minimised the temperature variation of inductance.¹⁴ In the critical oscillator a similar coil was placed in parallel with the Sayce Briscoe dielectric constant cell of about 50 mmfd capacity and the measuring precision condenser. The measuring condenser had a capacity of about 500 mmfd. Coupled to this were two sets of compact tuning drives consisting of a set of toothed double wheels having interconnected springs to avoid backlash and fitted with a rotating scale disc and a graduated vernier strip. The precision condenser was thus capable of fine adjustments and even small settings could be measured accurately.

The true capacity of the test cell was obtained after calibrating the measuring condenser for linearity as indicated by Smyth³¹ and applying corrections for leads^{12, 29} and finally for the replaceable capacity by evaluation of the zero capacity C_0 .²² The dielectric constants of the solutions were evaluated from the standard equation

$$\epsilon_s = \frac{C_0 - C_S}{C_0 - C_A}$$

Densities of the dilute benzene solutions were obtained using an Ostwald Sprengel pycnometer with ground-in caps closing both ends. Refractive indices of solutions of various concentrations were straightway read from an Abbe refractometer. The molar refraction obtained from measurements was compared with that calculated using the additivity of bond refractions,¹⁰

The polarisation ${}_T P_{\infty}$ at infinite dilution of the solute was obtained from the average of the calculated values of Hedestrand constants, α and β given in the following tables.

TABLE I
Tetrahydropyran in Benzene—Temp. $35^{\circ} \pm 0.005^{\circ}$ C.

Concentration in mole fractions	Dielectric constant	Density	α	β
0.000000	2.2535	0.86278
0.004962	2.2732	0.86298	1.772	0.0429
0.012068	2.2927	0.86325	1.404	0.0425
0.018338	2.3115	0.86347	1.407	0.0451
0.037196	2.3714	0.86425	1.370	0.0433
0.073825	2.4848	0.86550	1.441	0.0432

${}_M R_D$ measured = 24.2 c.c.

${}_T P_{\infty}$ = 78.33

${}_M R_D$ calculated = 24.92 c.c.

μ = 1.63D

TABLE II
Dihydropyran in Benzene—Temp. $35^{\circ} \pm 0.005^{\circ}$ C.

Concentration in mole fractions	Dielectric constant	Density	α	β
0.000000	2.2535	0.86278
0.026371	2.3165	0.86480	1.060	0.089
0.053563	2.3851	0.86673	1.091	0.085
0.083208	2.4600	0.86881	1.101	0.084
0.099261	2.5009	0.87010	1.101	0.089
0.130717	2.5760	0.87232	1.064	0.089

${}_M R_D$ measured = 24.1 c.c.

${}_T P_{\infty}$ = 63.09

${}_M R_D$ calculated = 24.45 c.c.

μ = 1.38D

DISCUSSION

Allen and Hibbert¹ suggested that the six-membered tetrahydropyran ring is diplanar and if this be so then a puckering of the ring will enable the valence bonds to assume any convenient angle so that any strain on these bonds will be very small. Recently DeVries Robles,¹¹ in discussing the

effect of cyclisation of the ethylene oxide homologues on the electric moments, calculated the strain in each of the molecules from simple energy considerations and assigned to each the most probable structure. According to him the strain is zero for both tetrahydropyran and dioxan, both having a strainless structure, on account of the great freedom of the ring. The molecules can occur both in the stiff chair form and in the mobile form. In the mobile form are a continuous series of crossed structures of which the boat form is a particular position.

The evidence of various physical measurements leaves no doubt that the natural valency angle of oxygen is close to the tetrahedral angle of 109° . Thus an angle of 110° has been obtained in the crystal structure of ice.² Pople²⁷ using the theory of molecular and equivalent orbitals, obtains for the oxygen valency angle an equilibrium value of 105° , both hybridization parameters being close to the value that may be expected for tetrahedral orbitals, originally introduced by Pauling²⁶ in 1931. Thus the equivalent orbital description of the water molecule assigns it an approximately tetrahedral character, with bond orbitals pointing in two of the directions and equivalent lone pairs in the other two. This may be regarded as a theoretical foundation for the tetrahedral model used by Bernal and Fowler.⁶ A study of the collision areas of ethers points in the same direction¹⁹ and the infra-red spectrum of water vapour has led to various values ranging from 105° to 110° .^{24,25} Bennet^{4,5} taking the C-C and C-O distances in dimethyl ether as 1.54 Å and 1.40 Å respectively and the C-C bond moment as 0.2 D obtained a value of 1.01 D for the C-O bond moment. The moment of dimethyl ether then leads to a valency angle of 115° (see however Gent¹³). Yet an analysis of the dipole moments of some diphenyl ethers indicates that, in these substances, the angle is probably larger than the tetrahedral value and Hampson¹⁸ has calculated a value of 124° to 132° for the oxygen valency angle in these ethers. However, there is no justification for supposing that the valency angle of oxygen in other compounds is necessarily the same as in diphenyl ethers. Sutton and Brockway³⁰ find $105^\circ \pm 5^\circ$, $111^\circ \pm 2^\circ$, $111^\circ \pm 4^\circ$ and $110^\circ \pm 5^\circ$ for the oxygen valence angle in F_2O , Cl_2O , $(CH_3)_2O$ and dioxan respectively.

In the case of tetrahydropyran, using the bond moment values and an oxygen valence angle of 93° , Allen and Hibbert (*loc. cit.*) calculate a dipole moment value agreeing with their experimental value of 1.87 D, while Gent (*loc. cit.*) using their experimental value obtains for the valence angle a value of 111° . This has been obtained using a bond moment of 0.4 D for the C-H bond and 1.15 D for the C-O bond. Allen and Hibbert's calculations for a valence angle of 110° leads to a moment of 1.65 D

a value which conforms to our experimental observations. De Vries Robles (*loc. cit.*) reports for tetrahydropyran a valence angle of 111° while Beach³ has reported a similar value from experimental results with tetramethylene oxide. Taking all factors into account we may then consider that the valence angle of oxygen in these compounds is about 111° .

In the case of dihydropyran, the introduction of a double bond alters the moment appreciably. The ring system will tend to planarity thus leading to a reduced moment. This is clearly shown by the experimental value of 1.38 D.

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SUMMARY

The dipole moments of tetrahydropyran and dihydropyran have been obtained from measurements of dielectric constants of benzene solutions using a heterodyne beat method and following Hedestrand's method of extrapolation for arriving at the value for total polarisation. The results obtained have been discussed in relation to the structure of these compounds.

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