

DIPOLE MOMENTS OF SOME FURAN DERIVATIVES*

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Received February 25, 1964

THE five-membered heterocyclic compound furan possesses quite a few interesting properties on account of its structural features. An examination of the dipole moments of its derivatives should, therefore, be of some interest. A non-alternant aromatic system with a lone pair of electrons can be expected to show some deviation from the alternant type in interaction with neighbouring groups. In the present study we examine the dipole moments of 2-methyl, 2-hydroxymethyl and the tetrahydro-2-hydroxymethyl derivatives.

EXPERIMENTAL

Materials

Benzene purified by standard methods was the solvent used. The furan compounds were samples received from the Imperial Chemical Industries, dried and fractionated in all-glass vessels using only the middle fraction of a freshly distilled sample. The physical characteristics of the compounds used were: 2-Methyl furan: b.p. 63–64° C./760 mm., 2-Hydroxymethyl furan: b.p. 171–172° C./760 mm. Tetrahydro-2-Hydroxymethyl furan: b.p. 177–178° C./760 mm.

Method

A heterodyne beat method using an apparatus following Hudson and Hobbs⁷ was adopted for the dielectric constant measurements in a Sayce-Briscoe cell. Densities were measured with an Ostwald-Sprengel pycnometer with ground glass caps. Refractive indices were measured with an Abbe Refractometer and molar refractions were compared with the additivity of bond refractions by Denbigh's method.² Total polarisations were obtained by the Hedestrand method.⁶

The experimental results are collected in Tables I, II and III.

* Based on the M.Sc. thesis of S. S. to the Madras University.
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TABLE I

Measurements with 2-methyl furan in benzene solution at $35 \pm .005^\circ \text{C}$.

Mole fraction of solute	Dielectric constant	Density	α	β
0.00000	2.2535	0.86278
0.01132	2.2600	0.86340	0.255	0.064
0.02958	2.2698	0.86441	0.245	0.064
0.05531	2.2858	0.86585	0.259	0.064
0.10144	2.3064	0.86835	0.231	0.064
0.16176	2.3365	0.87170	0.227	0.064
			Mean 0.243	0.064
Molar Refraction:				
Calculated	23.98 c.c.			
Measured	23.24 c.c.			
Total Polarisation:	34.56 c.c.		Dipole Moment: $0.72 \pm .01 \text{ D}$	

TABLE II

Measurements with 2-hydroxymethyl furan in benzene solution at $35 \pm .005^\circ \text{C}$.

Mole fraction of solute	Dielectric constant	Density	α	β
0.00000	2.2535	0.86278
0.00626	2.2836	0.86432	2.134	0.286
0.01557	2.3403	0.86674	2.758	0.245
0.03184	2.4245	0.87124	2.381	0.308
0.04724	2.5080	0.87500	2.390	0.300
0.05132	2.5300	0.87603	2.037	0.299
			Mean 2.340	0.288
Molar Refraction:				
Calculated	25.53 c.c.			
Observed	22.90 c.c.			
Total Polarisation:	105.0 c.c.		Dipole Moment: 2.00 ± 0.02	

TABLE III
 Measurements with tetrahydro-2-hydroxymethyl furan
 in benzene solution at $35.0 \pm 0.005^\circ \text{C}$.

Mole fraction of solute	Dielectric constant	Density	α	β
0.00000	2.2535	0.86278
0.00530	2.2891	0.86388	2.980	0.242
0.01109	2.3344	0.86505	3.238	0.238
0.02065	2.4000	0.86717	3.148	0.247
0.02746	2.4512	0.86851	3.195	0.242
0.04309	2.5549	0.87195	3.104	0.247
			Mean 3.133	0.246
Molar Refraction:				
Calculated	22.55 c.c.			
Observed	26.47 c.c.			
Total Polarisation :	134.4 c.c.		Dipole Moment $2.33 \pm 0.02 \text{ D}$	

TABLE IV
Pi moments for furan

C—O moment	Reference	Calculated moment	Pi moment
2.3	(4)	2.62	1.91
1.7	(3)	2.04	1.33
0.86	(11)	1.23	0.52
1.57*	(10)	2.24	1.53

* Modified Groves and Sugden Method *vide* Ref. 10.

DISCUSSION OF RESULTS

Any examination of the dipole moments of the derivatives has to be in relation to that of the parent compound itself. It is interesting to see here how experimental values compare with calculations including the Groves and Sugden method⁴ for computing induced moments. Even experimental values show variations from 0.63⁸ to 0.72⁵. In the theoretical calculations, sigma bond moments may be computed by vectorial addition while pi moments are evaluated by the method of molecular orbitals.¹ Sutton and his associates¹² obtain for the pi moments a value of 1.15 leading to a moment for furan of only 0.2. Allowing for induced moments and using different values of the C—O bond moment, varying values could be obtained for the pi moment (Table IV). The second and last values are fairly close to the values of Sutton (*loc. cit.*). It is clear that the final value depends on the initial choice for bond moment. Nonetheless, one can reasonably infer from the magnitude of the value that there is appreciable delocalisation of the electrons and ionic terms are not negligible even in the unsubstituted furan.

A dipole moment of 0.73 for 2-methyl furan shows that the methyl group causes little disturbance to the system and is comparable to the influence in an alternant aromatic system. The *p* orbital characteristics of the system of three hydrogens interacting with the ring pi electrons can have the effect of a shortened C-C bond with small changes in the induced moments so that the net result in the heterocyclic system is small. Our values for the compound are comparable to those reported by Syrkin.¹³

Differences may, however, be expected both by the introduction of a hydroxy methyl group in place of the methyl and the reduction of this compound to a saturated ring system. One possible complication with hydroxy compounds is the association through intermolecular hydrogen bonding. Our observation within the range of concentrations studied indicates that this is absent and we can consider the moment as that of the pure alcohols. A structural feature that has to be reckoned in these is the variety of conformations that are possible on the basis of restricted rotation about the C—C bond outside the ring. These are indicated in Fig. 1. Calculation of dipole moments by the Groves and Sugden method indicates that the favoured configuration is single bond *cis* and the molecule may be said to conform to a synclinal form.⁹ The stabilisation of this form will be facilitated by hydrogen bonding of the hydroxyl hydrogen with the oxygen of the ring (5-membered ring system).

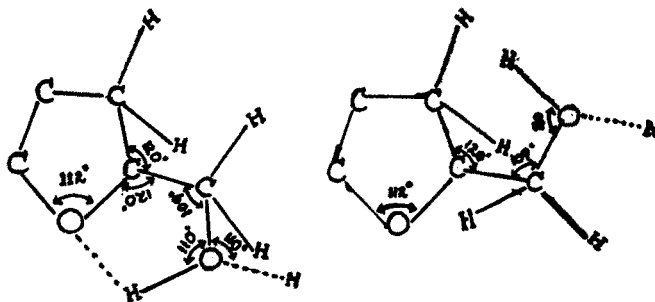


FIG. 1

The conversion to a saturated ring in the tetrahydro alcohol does not seem to interfere with this intramolecular hydrogen bonding and the moment observed is similarly in conformity with calculated values for this configuration.

We may conclude from our observations that in these alcohols structural features favour the formation of an intramolecular hydrogen bond with the result that there is no association through intermolecular hydrogen bonding. Spectroscopic studies will be interesting.

SUMMARY

The dipole moments of three furan compounds studied in benzene solution indicate the hyperconjugation effect of the methyl group and the existence of the alcohols primarily in the *cis* conformation (synclinal) with intramolecular hydrogen bonding involving the ring oxygen. The moments obtained are 0.72, 2.00 and 2.33 for the methyl, hydroxymethyl and the tetrahydroxymethyl derivatives in the 2 position.

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