

THE APPARENT DIPOLE MOMENTS OF CERTAIN SUBSTITUTED BIPHENYLS

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THE dipole moments in solution of a number of biphenyl derivatives have been studied by a number of workers.^{6, 12, 14-16, 24} Values for three compounds not studied previously are reported here.

EXPERIMENTAL

o-Hydroxy biphenyl.—A Eastman practical grade sample was recrystallized from petroleum ether; m.p. 56° C.

o-Methoxy biphenyl.—This was prepared as reported in a previous paper⁵; f.p. 29° C.; b.p. 273.5° C.; $n_D^{30.5}$: 1.6052; $d_4^{30.5}$: 1.0409.

pp'-Dihydroxy biphenyl.—A Eastman practical grade sample was recrystallized from alcohol; m.p. 274° C.

The solvents, benzene and dioxan were purified by standard methods¹⁸; Their physical constants were: Benzene—b.p. 80.1° C.; n_D^{35} : 1.4920; d_4^{35} : 0.86278; Dioxan—b.p.: 101° C.; n_D^{35} : 1.4155; d_4^{35} : 1.0169.

Dielectric constants were measured by the heterodyne beat method,¹⁹ refractive indices with a Pulfrich refractometer and densities with pycnometers. The required temperature, 35° C., was maintained by an oil thermostat with an electronic relay.¹

Tables I to III give the data required for the calculation⁹⁻¹¹ of the apparent moment values.

DISCUSSION

Table IV gives the dipole moment values obtained in these experiments together with those of the corresponding benzene derivatives.

TABLE I
o-Hydroxy biphenyl in benzene

Weight fraction (<i>w</i>)	Dielectric constant (ϵ)	Refractive index (n_D)	n_D^2
0.000000	2.2535	1.4920	2.2262
0.021962	2.2894	1.4933	2.2301
0.036510	2.3181	1.4947	2.2342
0.052344	2.3490	1.4966	2.2397
0.064292	2.3562	1.4981	2.2443

$$\mu = 1.63 \text{ D.}$$

TABLE II
o-Methoxy biphenyl in benzene

Weight fraction (<i>w</i>)	Dielectric constant (ϵ)	Refractive index (n_D)	n_D^2
0.000000	2.2535	1.4920	2.2262
0.019443	2.2786	1.4941	2.2323
0.039441	2.3023	1.4957	2.2370
0.052536	2.3296	1.4966	2.2399
0.058352	2.3375	1.4977	2.2431

$$\mu = 1.38 \text{ D.}$$

Treating the biphenyl derivative in the first two cases as an *ortho*-substituted benzene, the higher values found in both these biphenyl derivatives may be partly attributed to both inductive and mesomeric effects of the second phenyl ring, and the almost identical increments support such an inference.

TABLE III
pp'-Dihydroxy biphenyl in dioxan

Weight fraction (<i>w</i>)	Dielectric constant (ϵ)	Refractive index (n_D)	n_D^2
0.000000	2.1778	1.4147	2.0012
0.0047177	2.1977	1.4163	2.0049
0.0112940	2.2253	1.4174	2.0089
0.0191310	2.2512	1.4191	2.0139
0.0270620	2.2922	1.4211	2.0195

$\mu = 2.31$ D.

TABLE IV

Compound	Solvent	μ_{solution} in D	$\mu_{\text{benzene compound}}$
<i>o</i> -Hydroxy biphenyl	Benzene	1.63	1.49
<i>o</i> -Methoxy biphenyl	Benzene	1.38	1.25*
<i>pp'</i> -Dihydroxy biphenyl	Dioxan	2.31	2.47†

* Reference 22.

† Hydroquinone in ether.¹⁸

It will be interesting to study these apparent values in relation to the orientation of the benzene planes, since in *ortho*-substituted biphenyls there is a good chance of having the phenyls at different planes. The Smallwood-Herzfeld-Frank equations,^{8,20} utilized recently by Littlejohn and Smith,¹⁵ may be used:

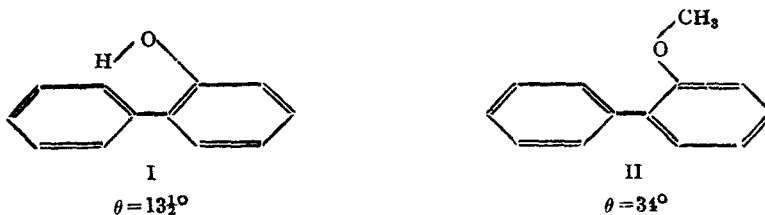
$$\mu_x = \mu\alpha \frac{\epsilon_a + 2}{3\epsilon_b r^3} (3 \cos^2\theta - 1)$$

$$\mu_y = \mu\alpha \frac{\epsilon_a + 2}{3\epsilon_b r^3} (3 \sin\theta \cos\theta)$$

where μ_x and μ_y are the components of the induced moment respectively parallel to and at right angles to the inducing moment μ ; α is the polariza-

bility of the polarizable medium, ϵ_a and ϵ_b are the dielectric constants of the polarizable system and of the medium between this and the primary dipole respectively, r is the distance between the dipole and the polarizable centre and θ the angle between μ and r . A monosubstituted biphenyl molecule is regarded as the corresponding derivative of benzene to which another polarizable group, *viz.*, a benzene ring has been attached. The polarizable centre of the latter is at the middle of the unsubstituted ring, and α the polarizability of benzene, which equals 12.5×10^{-24} in the plane of the ring and 6.25×10^{-24} at right angles to it.⁴ An approximation made by Littlejohn and Smith—also made here—is that both ϵ_a and ϵ_b are taken equal to the dielectric constant of benzene.

The inducing dipole in *o*-hydroxy biphenyl is taken to be the apparent moment of phenol in benzene solution (1.49 D). The value for anisole (1.25 D) is used correspondingly for *o*-methoxy biphenyl. The distance r is that between the centre of the unsubstituted ring and the centre of the oxygen atom. Since the dipoles of phenol and anisole are not acting on the C—O bonds, a further approximation introduced in the calculation was to consider the $\mu_{\text{resultant}}$ in these compounds as acting at $66\frac{1}{2}^\circ$ to the C—O bond.²¹ The conformations considered for the two cases and the values for θ are given below:



A study of scale models of the molecules makes it necessary for the methyl group of the methoxy function to be away from the unsubstituted phenyl ring to avoid steric interaction. Diagrams drawn to scale gave the value for r as 3.77 Å. Calculations led to the values which are given in Table V.

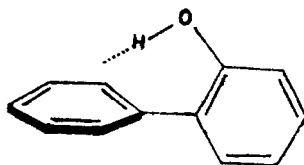
The observed value for *o*-hydroxy biphenyl in benzene solution is thus close to the one calculated for the rings at right angles. This would indicate, apart from possible errors, that a non-coplanar disposition of the rings is favoured in *o*-hydroxy biphenyl. Besides steric considerations (a molecular model constructed points to a definite though small steric repulsion), this may also be because an orthogonal disposition would favour an interaction between the proton of the phenolic group and the unsubstituted benzene ring.

TABLE V

Compound	Disposition of benzene rings	$\mu_{\text{calculated}}$	μ_{observed}
<i>o</i> -Hydroxy biphenyl	Coplanar	1.892 D	1.63 D
	Orthogonal	1.639 D	
<i>o</i> -Methoxy biphenyl	Coplanar	1.445 D	1.38 D
	Orthogonal	1.505 D	

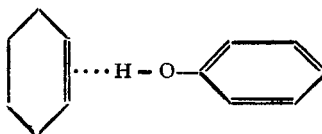
Two possibilities of such interaction seem to exist. Work on the infrared spectra of the compound led Wulf, Liddel and Hendricks²⁵ to state that "with the two rings swung far out of a common plane the first carbon atom of the *ortho*-substituted ring lies closest to the hydroxyl hydrogen and if this nearby carbon atom exercises an appreciable proton-attraction, this would lead to a *cis*-form and could give rise to two peaks" in the 6500–7500 cm.^{-1} region, as was actually observed by them.

The other alternative is that there is an attractive interaction between the proton of the phenolic group and the π -electron system of the unsubstituted benzene ring. For maximum interaction leading to a conformation of lowest energy will require the two rings to be at right angles (III):



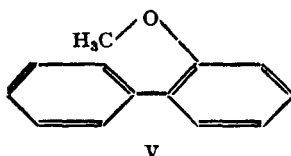
III

Such an interaction between a hydroxyl hydrogen and the π -electrons of a double bond was postulated by Mecke and Lüttke¹⁷ in an attempt to explain the higher moment of phenol in cyclohexene (IV):

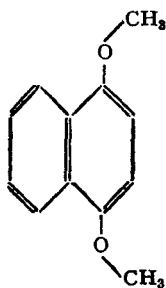


IV

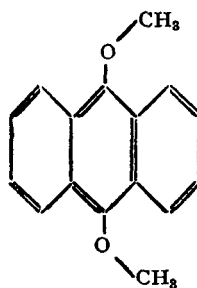
A comparison of the $\mu_{\text{calculated}}$ and μ_{benzene} values for *o*-methoxy biphenyl on the other hand indicates a possible coplanarity of the rings. This would seem to be surprising on account of the greater bulk of the $-\text{OCH}_3$ group compared to the $-\text{OH}$ group. A molecular model shows that, in order to avoid steric repulsions, the methyl of the methoxy group should point away from the unsubstituted phenyl as in II and that a minimal twisting of the C—C pivot bond to the extent of 30° will be all that is necessary. Also a possibility for a π -proton interaction does not exist. In view of the approximations involved in the calculations, we cannot choose between this conformation and a series of others with slight changes in the twist angles. Calculations based on a structure like V



where the $-\text{CH}_3$ group is nearer the unsubstituted ring do not lead to any significant improvement in the situation. Hence it may be concluded that in *o*-methoxy biphenyl, the benzene rings are nearer a coplanar than an orthogonal disposition and the methoxy group will tend to align itself for minimal intramolecular repulsion. Presumably the rotatory oscillation of the $-\text{OCH}_3$ group around the C—O bond is very much like that envisaged by Sutton²³ in the cases of dimethoxy naphthalene (VI) and dimethoxy anthracene (VII):



VI



VII

It may be pertinent at this juncture to consider relevant UV absorption data which would seem to support some of the foregoing tentative conclusions.

The sharp fall in absorption intensity of the K band points to the loss of coplanarity between the two rings. There is also a corresponding 'blue shift' in the λ_{max} . If the latter and the absorption intensity could be taken as a qualitative measure of increasing twist of the benzene rings from the

original common plane, *o*-hydroxy biphenyl has had more of it than *o*-methoxy biphenyl. This finding lends support to the arguments based on consideration of dipole data.

TABLE VI
Ultraviolet absorption data for biphenyls

Compound	Solvent	K band		Reference
		$\lambda_{\max.}$ ($m\mu$)	$\epsilon_{\max.}$	
Biphenyl	Light petroleum	248.0	17,000	Beaven ²
<i>o</i> -Methoxy biphenyl	<i>n</i> -Hexane	246.0	13,500	Burawoy ³
<i>o</i> -Hydroxy biphenyl	<i>n</i> -Hexane	244.2	12,500	Burawoy ³

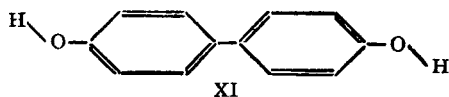
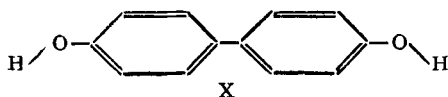
The apparent moment, in dioxan solution, of *pp'*-dihydroxy biphenyl is 2.31 D. Now, the analogous compound, hydroquinone, may have two extreme structures (VIII) and (IX):



If α is the angle of inclination of the moment of the —OH group and μ' its group moment, the resultant moment of hydroquinone, assuming unhindered rotation, may be shown to be given by:

$$\frac{1}{2} \mu' \sin \alpha$$

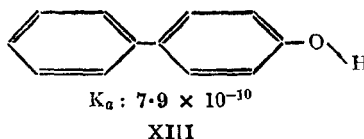
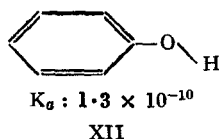
(Smith^{21a}). A calculation of the resultant of *pp'*-dihydroxy biphenyl by similar methods can be done. The corresponding structures considered are X and XI:



Here, the benzene rings in the biphenyl molecule have been assumed to be coplanar. On this assumption the calculated value for the compound in dioxan is 2.33 D, compared to the observed value of 2.31 D.

Thus there is a very close correspondence between the calculated and observed values. The assumption of coplanarity for the two benzene rings

would then seem to be sound. This is also corroborated by a consideration of the acidities of phenol and *p*-phenyl phenol⁷:



The greater acidity of *p*-hydroxy biphenyl is due to the mesomeric effect of the *para*-phenyl ring, which is possible only when there is a significant overlap of all the π -orbitals in the two rings—hence coplanarity will be favoured. And the addition of one more —OH group at the *para*-position of the unsubstituted benzene ring is not expected to cause any distortion of the plane of the molecule.

SUMMARY

The apparent electric dipole moments of *o*-hydroxy biphenyl, *o*-methoxy biphenyl and *pp'*-dihydroxy biphenyl have been determined. The values serve to point to the following structural features: (1) In *o*-hydroxy biphenyl the two benzene rings seem to be orthogonal and there seems to be an interaction between the proton of the —OH group and the π -electrons of the unsubstituted benzene ring. (2) In *o*-methoxy biphenyl the two benzene rings seem to be slightly tilted from the coplanar conformation. (3) In *pp'*-dihydroxy biphenyl the two benzene rings seem to be coplanar.

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