THE DIPOLE MOMENT OF DIMETHOXY AND DIETHOXY ANILINE

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The dipole moments of 2-amino-1 : 4-dimethoxy benzene and of 2-amino-1 : 4-diethoxy benzene have been studied in benzene and in carbon tetrachloride solution. The values of the moments are discussed in relation to the moments of the unsubstituted parent carbon compounds. The interaction between three groups of similar characteristics is considered in relation to their steric effects.

HYDROQUINONE and its methyl and ethyl ethers are well known instances[6] where the moments of two substituents in the para position do not cancel each other. It was felt that the introduction of a third substituent might show additional features similar to those of *p*-xylene derivatives. The present communication deals with the amino derivatives of the two quinol ethers

EXPERIMENTAL

The solvents used were purified as in the previous communication on para-xylene derivatives.[1]

2-aminol-1 : 4-diethoxy benzene: The Kodak sample was first decolourised by crystallisation from water in the presence of decolorising carbon and then recrystallised from distilled water. White flakes m.p. 86° C.

2-amino-1 : 4 dimethoxy benzene was also prepared in the same manner from a Kodak sample. White flakes, m.p. 81° C.

The measurements of dielectric constant were by a 'heterodyne beat method' as described earlier[1] and refractive indices and densities were also measured similarly. Care was needed to exclude light and air during re-crystallisations of these compounds.

The relevant experimental results are collected in Tables I and II below.

DISCUSSION OF RESULTS

In the parent compound, the existence of a dipole moment has been attributed to the presence of free rotation about the C_{aryl}—O bonds.[2] The introduction of a substituent group ortho to one of the ether groups can be

TABLE I

Measurements with 2-amino-1 : 4-dimethoxy benzene at $32 \pm 0.01°$ *C.*

Solvent	Weight fraction of solute	Density of solution	Refractive index of solution	Dielectric constant of solution
Benzene	0	0·86521	1·4934	2·2588
	0·005759	0·90390	1·4942	2·2692
	0·01226	0·90478	1·4948	2·2831
	0·01766	0·90680	1·4956	2·2868
	0·02351	0·90738	1·4962	2·2978
Carbon tetra-chloride	0	1·5705	1·4536	2·2155
	0·002941	1·6390	1·4540	2·2256
	0·004960	1·6376	1·4547	2·2285
	0·006410	1·6367	1·4550	2·2290
	0·007080	1·6362	1·4552	2·2300

TABLE II

Measurements with 2-amino-1 : 4-diethoxy benzene at $32 \pm 0.01°$ *C.*

Solvent	w	d	n	ϵ
Benzene ..	0	0·86521	1·4934	2·2588
	0·007344	0·90400	1·4935	..
	0·009795	0·90452	1·4942	2·2704
	0·01383	0·90500	1·4945	2·2835
	0·01783	0·90635	1·4948	2·2990
Carbon tetra-chloride	0	1·5705	1·4536	2·2155
	0·002871	1·6348	1·4538	2·2236
	0·006354	1·6327	1·4541	2·2286
	0·007018	1·6323	1·4545	2·2338
	0·007533	1·6320	1·4548	2·2368

expected to modify this picture. Here, too, it is worth studying how far the different methods of calculation of dipole moments lead to the same value. The results are presented in Table III below.

TABLE III

Dipole Moments of Dimethoxy aniline and Diethoxy aniline

Compound	Halverstadt-Kumler			
	$P_{2/\infty 0}$	M_{R}^{D}	$_0P_2$	Moment
2-Amino-1 : 4-dimethoxy benzene	.. 67·89	53·35	14·54	0·85
2-Amino-1 : 4-diethoxy benzene	.. 71·73	60·82	10·89	0·74

It is not our present purpose to consider the relative merits of the different approximations used in the evaluation of dipole moments, but, most of the previous studies on related compounds have used the Halverstadt-Kumler method and for comparisons, these values alone will be used. Everard and Sutton[3] have studied the dichloro and dibromo derivatives and these values together with those of the parent ethers are collected in Table IV.
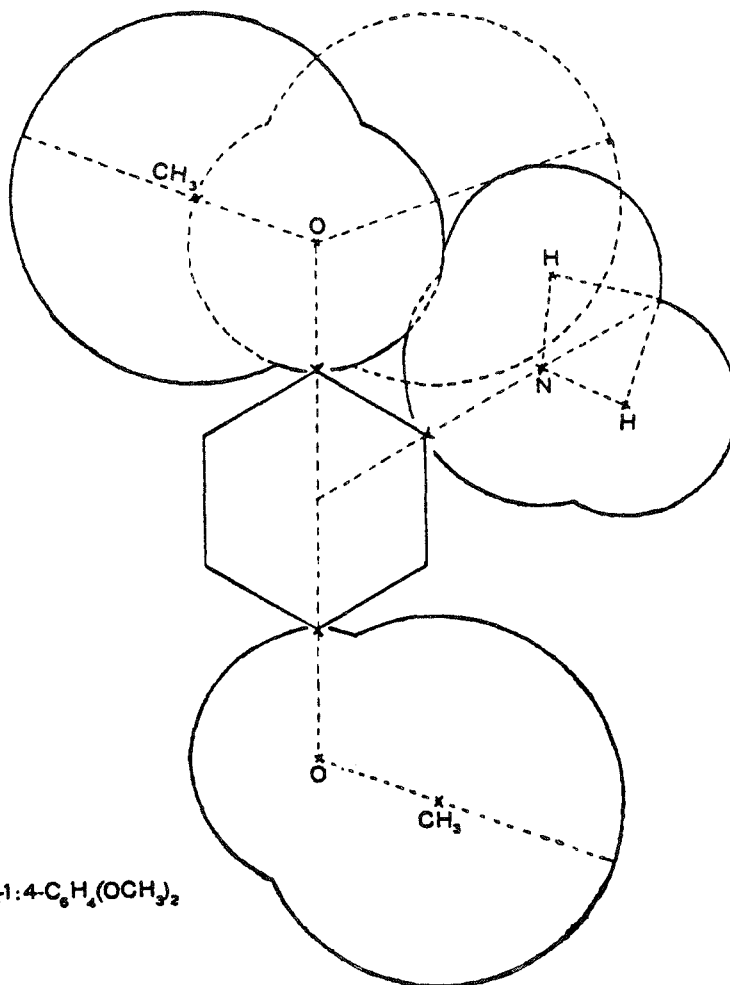
TABLE IV

Compound	Dipole moment	Reference
1 : 4-Dimethoxy benzene ˙	1·81 (1·70)	4 (5)
2 : 5-Dichloro-1 : 4-dimethoxy benzene ..	1·03	3 (a)
2 : 5-Dibromo-1 : 4-dimethoxy benzene ..	1·01	3 (b)
2-Amino-1 : 4-dimethoxy benzene ..	0·85	Present work
1 : 4-diethoxy benzene	1·76	4
2-Amino-1 : 4-diethoxy benzene ..	0·74	Present work

The alkoxy groups are well known examples of groups having appreciable mesomeric moments and this would naturally impose a certain degree of restraint on free rotation. The presence of any substituent on the 2 and 5 positions may be expected to further modify this and it is natural to expect

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TABLE V

Compound			Moment in Benzene	Moment in carbon tetrachloride
1: 4-Dimethoxy benzene	..	..	1·70	1·81
2-Amino-1: 4-dimethoxy benzene		..	0·85	1·37
2-Amino-1: 4-diethoxy benzene	..	..	0·74	1·21

FIG 1   2-NH$_2$-1:4-C$_6$H$_4$(OCH$_3$)$_2$

that the moments may be reduced by such substitution. This is clearly borne out by Table IV. The steric interaction which requires the groups to take up a multiplanar arrangement is also illustrated by Figures 1 and 2.
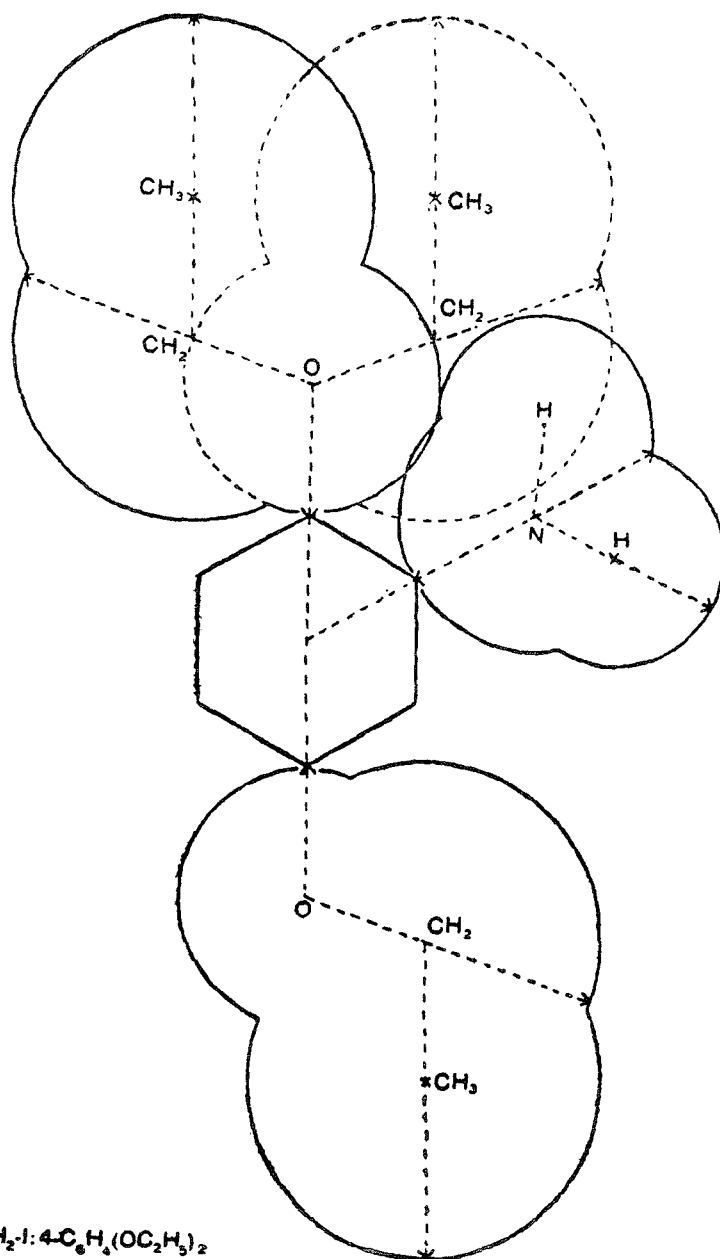

FIG. 2. $2 \cdot NH_2 \cdot 1 : 4 \cdot C_6H_4(OC_2H_5)_2$

In the parent ether itself, the presence of the two alkoxy groups in para position, by mutual action, may cause a reduction in the resonance effect and two extreme configurations are the cis and trans configurations. The former will be the more polar group but there is no compelling reason why the cis form should be favoured. Possibly, we are having here an instance of appreciable atom polarisation.[6]

Several instances of interactions between ortho substituents of this type have been reported with the mono ethers.[7] From their study of the fluoro, chloro and bromo anisoles and of chlorophenetole, Anzilotti and co-workers find that the ortho substituents take up what they call a ' trans-trans ' arrangement and a similar conclusion is reached by Smyth[8] from a study of di-tertiary butyl quinol dimethyl ethers (moment 1·42). In the presente instance also, a stable arrangement requires that one of the groups moves in a direction in the plane of the ring while the other moves in a direction perpendicular to the plane of the ring.

While the unsubstituted ether has the preferential cis configuration of the methoxy or ethoxy groups, a trans configuration is favoured in the amino derivatives by the possibility of hydrogen bonding between the amino group and the oxygen of the methoxy or ethoxy group which is possible only in this arrangement. Ortho methoxy phenols are known to indicate such interaction between the hydroxy group and the oxygen of the methoxy group.[9]
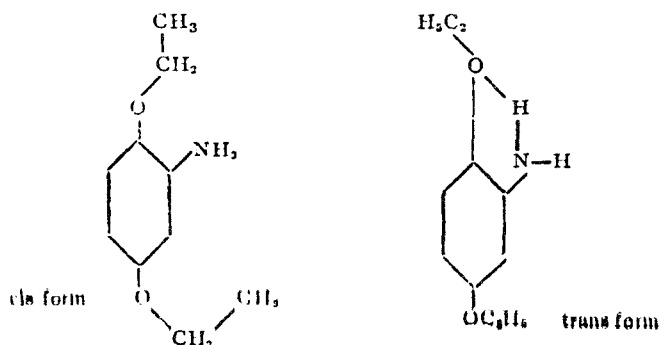
This spatial arrangement also results in a reduction in the effective moment of the compounds. The overall lowering is thus a cumulative one, the reduction in moment being greater in the ethoxy compound possibly by the stronger hydrogen bonding induced by the ethyl as compared to the methyl group. One consequence of the interaction is that the moment is reduced to a value below that of aniline.

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ADDENDUM

It will be noticed from the figures that the difference in moments between the solution in benzene and in carbon tetrachloride is very large. The abnormality is with the carbon tetrachloride value. Apart from the usual difference that has been generally observed with the change in dielectric constant of solvent, even though the solvent is nonpolar, fine needle-shaped colourless crystals *which are not the same as the original compound dissolved* have been consistently obtained. The nature and identity of the compound has not yet been established but the formation of this new compound is at least in part responsible for the abnormal values obtained.