

DIPOLE MOMENTS OF SOME DERIVATIVES OF PARA-XYLENE—A POSSIBLE INTRAMOLECULAR HYDROGEN BONDING

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SYMMETRICALLY substituted derivatives of benzene have been of interest in all studies where the interest is in evaluation of the mesomeric moment as a modifying factor and in all of the studies with mesitylene and durene there is the tacit assumption that symmetrical substituents mutually cancel their moments and all abnormalities are attributed to the unsymmetrical substituent alone. As we had indicated earlier¹ substituted *para*-xylenes provide us with a crucial test. The analogy of trihalogenophenols and anilines where the halogen moments do not cancel each other is a pointer for a more complete analysis.

EXPERIMENTAL

Materials Used

The solvents used in the investigation were purified by standard methods and stored in a dry condition in stoppered brown bottles over suitable drying agents. The purity was tested by their physical properties including ultraviolet absorption.

The chloroxylenes were prepared by the method of Wahl,¹⁹ the mono- and di-derivatives being separated by careful fractionation, dried over potassium hydroxide where the product was a liquid and the solid derivative was recrystallised before use.

The Bromoderivatives were prepared by an extension of the method of Horning⁷ using iodine as catalyst. The products were dried over anhydrous calcium chloride, distilled and then dried over anhydrous copper sulphate and then fractionated. The dibromo-compound was prepared by the method of Marzin.⁹

The iodocompounds were prepared by the method of Varma.^{17, 18}

The physical characteristics of the compounds prepared are given in Table I.

TABLE I

Physical characteristics of the compounds used
(All compounds are derivatives of 1 : 4-dimethyl benzene)

Compound (substituent only given)	B.P. °C./760 mm.	d_4^{25}	n_D^{25}
2-Chloro	.. 184	1.053	1.5219
2-Bromo	.. 199-200	1.339	1.5452
2-Iodo	.. 230	1.585	1.5888
2-Nitro	.. 234-237	1.123	1.5368
2-Amino	.. 213-215	0.971	1.5528
2: 5-Dichloro	.. m.p. 71° C.
2: 5-Dibromo	.. „ 75
2: 5-Diiodo	.. „ 104
2: 5-Dinitro	.. „ 142
2: 6-Dinitro	.. „ 123

Dipole moment measurements were made by a heterodyne beat method using a modified Jen-Yuan Chain⁹ apparatus. The liquids and solutions for the measurements were kept in a modified Sayce-Briscoe cell.¹¹

Dipole moments were measured in several solvents and the relevant experimental data are collected in Tables II to XII.

DISCUSSION OF RESULTS

It will be convenient if we divide the analysis of our results into three sections: 2-substituted xylenes, 2-5 and 2-6 disubstituted xylenes and solvent influences.

The introduction of a substituent in the 2-position changes the symmetry of the molecule from the D_{2h} symmetry of *p*-xylene to one of a very much lower one. Scale model drawings as well as models of the Catlin type clearly indicate that in all these compounds a multiplanar arrangement is essential.

TABLE II

Measurements with 2-chloro 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^6$	720	1250	1560	1943	541	865	1059	1437
$\epsilon \times 10^4$.. 22798	23046	23194	23387	22393	22542	22644	22838
$n^2 \times 10^4$.. 22314	22344	22362	22386	21157	21175	21184	21198
α	..	2.85				4.39		
ν	..	0.21				0.45		
Pure solvent								
$\epsilon \times 10^4$..	22588				22155		
$n^2 \times 10^4$..	22300				21130		

TABLE III

Measurements with 2-bromo 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	750	1046	1528	1956	536	945	1156	1542
$\epsilon \times 10^4$.. 22746	22894	23141	23342	22337	22529	22631	22827
$n^2 \times 10^4$.. 22317	22335	22364	22387	21153	21175	21184	21206
		α 2.08		ν 0.23		α 3.35		ν 0.42

The changes in moment from the corresponding benzene derivative has been attributed as mentioned earlier to changes in mesomerism and a reduced resonance contribution. As we had indicated earlier¹ this is by no means the only picture. Superimposed on this multiplanar structure if other electrical interactions are brought into play, the role of symmetry becomes quite significant. One such change is the interaction between the methyl

TABLE IV
Measurements with 2-iodo 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	565	782	995	1315	464	653	947	1332
$\epsilon \times 10^4$.. 22673	22769	22872	23021	22066	22199	22306	22418
$n^2 \times 10^4$.. 22317	22329	22341	22360	21153	21164	21180	21201
	α 1.46		ν 0.28		α 2.38		ν 0.49	

TABLE V
Measurements with 2-nitro 1:3-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	555	1042	1398	2252	743	1256	1545	1857
$\epsilon \times 10^4$.. 23337	23608	23797	24248	23708	23976	24125	24277
$n^2 \times 10^4$.. 22314	22320	22324	22330	21163	21169	21172	21176
	α 13.44		ν 0.24		α 20.85		ν 0.44	

TABLE VI
Measurements with 2-amino 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	758	2071	3420	5150	432	731	1759	1990
$\epsilon \times 10^4$.. 22856	23262	23537	23688	22446	22560	22825	22879
$n^2 \times 10^4$.. 22324	22350	22370	22406	21152	21159	21195	21207
	α 4.05		ν 0.35		α 4.23		ν 0.43	

TABLE VII

Measurements with 2:6-dinitro 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	865	1054	1442	1730	565	752	995	1210
$\epsilon \times 10^4$.. 22968	23086	23325	23504	22551	22153	22276	22382
$n^2 \times 10^4$.. 22321	22333	22357	22379	21159	21171	21186	21198
	α 4.46		ν 0.25		α 7.00		ν 0.53	

TABLE VIII

Measurements with 2:5-dichloro 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	545	1092	1630	2125	440	687	1025	1236
$\epsilon \times 10^4$.. 22589	22591	22598	22602	22157	22161	22165	22170
$n^2 \times 10^4$.. 22345	22360	22371	22403	21215	21228	21249	21258

TABLE IX

Measurements with 2:5-dibromo 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	562	1110	1680	2251	329	650	1125	1301
$\epsilon \times 10^4$.. 22592	22598	22604	22606	22159	22162	22169	22172
$n^2 \times 10^4$.. 22351	22370	22381	22402	21217	21230	21251	21260

TABLE X

Measurements with 2:5-di-iodo 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	495	996	1323	1956	400	699	1086	1221
$\epsilon \times 10^4$.. 22590	22596	22602	22605	22157	22160	22164	22169
$n^2 \times 10^4$.. 22342	22359	22370	22382	21212	21228	21247	21258

TABLE XI

Measurements with 2:5-dinitro 1:4-dimethyl benzene

Solvent	Benzene				Carbon tetrachloride			
Weight Fraction of Solute $\times 10^5$	510	1017	1520	2034	390	690	1008	1358
$\epsilon \times 10^4$.. 22591	22602	22608	22611	22158	22160	22167	22171
$n^2 \times 10^4$.. 22382	22390	22395	22401	21215	21229	21252	21261

group and the substituents ortho to it. The delocalisation of the C-H bond electrons gives the group an orbital with pi-character which should be able to interact with the pi-electron system in the groups in an adjacent position. In mesitylene and durene the interaction can be symmetrically distributed so that the statistical averaging cancels out this contribution and so the change fortuitously fails to be noticed. This is not the case with *p*-xylene and hence we can expect abnormal values here. A comparison of derivatives with progressive additions of methyl group symmetrically will bring this out. This is done in Table XIII.

It is generally assumed that a C-H hydrogen does not participate in any hydrogen bonding. This is by no means an accurate picture. Mesitaldehyde having a dipole moment slightly higher than benzaldehyde has been attributed by Sutton and co-workers¹⁵ to steric hindrance while Smith suggests it to a possible hydrogen bonding of the C-H hydrogen of the methyl group

TABLE XII

Dipole moments of 1:4-dimethyl benzene derivatives

Substituent and position in ring	Dipole moment in benzene Debyes		Dipole moment in carbon tetrachloride Debyes	
	G	H and B	G	H and B
2-Chloro ..	1.79	1.93	1.72	1.84
2-Bromo ..	1.72	1.85	1.70	1.82
2-Iodo ..	1.54	1.65	1.53	1.63
2-Nitro ..	4.15	4.46	4.10	4.34
2-Amino ..	1.86	2.12	1.99	2.13
2:6-Dinitro ..	2.65	2.85	2.60	2.79
2:5-Dichloro ..	0	..	0	..
2:5-Dibromo ..	0	..	0	..
2:5-Diiodo ..	0	..	0	..
2:5-Dinitro ..	0	..	0	..

G: Values calculated using Guggenheim's method.

H and B: Values calculated by the method of Harris and Brush.

to the carbonyl oxygen especially when one takes into account the shift in the carbonyl frequency to 1687 from the value in benzaldehyde.¹²

Coulson has shown that while for convenience one may separate hydrogen bonding into electrostatic interaction, delocalisation effects, repulsive forces and dispersion forces, any such separation is artificial.⁵ The absorption spectrum of *o*-toluidine²⁰ clearly indicates a restriction in the free rotation of methyl group as also an interaction with the nitrogen showing hydrogen bonding of the type C-H...N. Again, spectral studies on *n*-propyl, *sec*-butyl and *isobutyl* chlorides and bromides show evidence of the *gauche* form of the rotational isomers with interaction between the methyl and halogen groups.¹⁶ Chena and Petrakaus⁴ have shown that such interactions have to be reckoned even with methyl groups among themselves. All these observations clearly indicate that our dipole moments are consistent with a picture

TABLE XIII

Dipole moments of benzene derivative and the effect of progressive methylation

Parent Hydrocarbon	Substituent						CHO
	Cl	Br	I	NH ₂	NO ₂		
Benzene	1.56	1.52	1.38	1.53	{3.97- 4.01	2.92	
Toluene (ortho substitution)	1.43	1.44	1.21	1.58	3.72	..	
<i>p</i> -Xylene	1.79	1.72	1.54	1.96	{3.91- 4.15	..	
Mesitylene	1.52	..	{1.40- 1.45	{3.65- 3.71	2.96	
Durene	1.55	..	1.45	{3.39- 3.62	..	

of hydrogen bonding between methyl hydrogens and the substituent in the ortho position. If this is not observed with mesitylene and durene derivative, the difference arises from a cancellation of the contribution of two symmetrically distributed vectors to the total moment and only the residual moment from other causes happens to be present. Further evidence from spectral data will be communicated later. The closeness of the dipole moment values of the *ortho*-toluene and *p*-xylene derivatives is significant and we can also infer that in these compounds the moment of the C-H bond is small (about 0.4) and also that hydrogen is the positive end of the dipole.

In the halogen series, one can expect that steric effects should be more important than electrostatic ones as we pass from chlorine to iodine. This is also shown by the trends in the dipole moments. Steric effects are dominant in the bulky iodine atom which also has little tendency to hydrogen bonding.

Turning to symmetrical disubstitution products, we observe that all the 2 : 5 dihalogeno and dinitro-compounds studied indicate a zero moment as may be expected. The dissymmetry introduced by the substituent in position 2 is destroyed by introducing the same group in position 5 and as expected,

the compounds have the characteristics of molecules with a centre of symmetry, more than one axis of symmetry and three planes of symmetry as the parent compound. Though the dipoles of the bonds are not of the ideal type, they are sufficiently close to treat the molecules as quadrupoles with the characteristics described by Böttcher.³ The similarity between the bromo, chloro and methyl groups is also shown by what has been loosely described as the 'Durene Effect'.⁶ Of all the disubstituted xylenes studied, the 2 : 6 derivative stands apart. The compound is of a lower order of symmetry, exhibits a definite moment but lower than the toluene or benzene derivatives. It is interesting to compare the values with those reported by Bell and Buck² for the ditertiary butyl dinitro-compounds. While the 2 : 5 dinitro compounds of the two series are similar in having zero moment, the 2 : 6 compounds show some difference. This difference can arise from two causes: The steric effects should be more pronounced in the ditertiary butyl compound and the position of the methyl groups is unfavourable for electrostatic interactions with the oxygen of the neighbouring nitro group. Also the polarisability and group moments of the methyl group is less than that of the *t*-butyl group but the polarisable centres are located nearer the ring in the methyl derivatives. The overall result is a higher moment in the xylene derivative. The resultant moment through the hydrogen bonding on either side of the methyl group has the effect of reduction in the moment in the corresponding toluene derivative. Spectroscopic studies which will be communicated later also indicate this aspect.

A factor that has to be reckoned in all the examples studied is the contribution of atom polarisation. It is recognised that there is no direct correlation between electronic and atom polarisation and empirical corrections often used are inadequate.¹³ There is some evidence that atomic polarisation is a function of the size and number of dipoles in the molecules, and the bending and stretching of bonds attached these dipoles but there is no additive behaviour thus leading to uncertainties.¹⁴ Further, as Paoloni¹⁰ has shown in his study of benzoquinone, deformation of lone pair orbitals by dipolar groups can induce a charge asymmetry modifying the dipole moment. Such a trend is not unlikely in the compounds under study.

SUMMARY

The dipole moments of mono- and disubstituted *para*-xylene derivatives have been measured in benzene and other solvents. The results show clearly that there is interaction between methyl hydrogen atoms and the substituents in the position ortho to the methyl. A comparison with mesitylene and durene derivatives indicates the need to consider

also the symmetry of the molecules and the uncertainties of atomic polarisation in a full understanding of the question.

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