

DIPOLE MOMENTS OF SOME SUBSTITUTED BENZENES AND PYRIDINES. PART III. CHLORO-AND BROMO ETHYL BENZENES

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ABSTRACT. The dipole moments of six ethyl substituted benzenes were determined in dilute solution in benzene. The effects of methyl and ethyl groups on other substituents in the benzene ring have been discussed in the light of the observed moments.

INTRODUCTION

A large number of methyl substituted benzenes have been investigated both in vapour and solution phases and their dipole moments determined. Using the dipole moment data, the structure of the methyl benzenes has been extensively discussed in regard to their effect on other substitutions and their inductive and resonance effects on the benzene ring itself (Smyth and Lewis, 1940). Similar investigations have not so far been carried out with ethyl substitution. Only two of these, namely, ethyl benzene and pentachloro ethyl benzene have been studied (Baker and Groves, 1939 and Smyth and Lewis, 1940). In the present investigation the dipole moments of six ethyl substituted benzenes have been determined in dilute solution in benzene, in order to understand the effect of replacing the methyl group with ethyl group in the benzene compounds.

EXPERIMENTAL

The experimental arrangement and the method of calculation are the same as described previously (Murty, 1957). All the ethyl benzenes were supplied by L. Lights and Co., England and were of analytical reagent standard of purity. The solvent benzene was also of A.R. grade of purity. The group moments and polarisabilities used in the calculation are given below.

Group	Moment	Polarisability $\alpha \times 10^{24}$ cc
Cl	1.55	2.51
Br	1.50	3.63
C_2H_5	0.58	4.21

RESULTS AND DISCUSSION

TABLE I
o-Chloro ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n_{12}^2	Δn^2	$\Delta n^2/W$
0.00962	2.2833	0.0193	2.007	1.49425	2.23277	0.00212	0.220
0.01397	2.2907	0.0267	1.908	1.49437	2.23315	0.00250	0.179
0.01954	2.2995	0.0355	1.817	1.49437	2.23315	0.00250	0.128
0.03522	2.3241	0.0601	1.707	1.49468	2.23406	0.00341	0.097
0.04420	2.3374	0.0734	1.661	1.49483	2.23451	0.00386	0.087
0.05164	2.3482	0.0842	1.631	1.49489	2.23470	0.00405	0.078

$(\Delta\epsilon/W)_D = 2.558$ $(\Delta n^2/W)_{W \rightarrow 0} = 0.080$
 $P_d = 49.6$ c.c. $\mu = 1.57$ D.

TABLE II
m-Chloro ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n_{12}^2	Δn^2	$\Delta n^2/W$
0.00730	2.2826	0.0186	2.544	1.49384	2.23155	0.00090	0.123
0.02024	2.3159	0.0519	2.563	1.49408	2.23227	0.00162	0.080
0.03132	2.3435	0.0795	2.537	1.49423	2.23273	0.00208	0.066
0.04107	2.3661	0.1021	2.485	1.49459	2.23380	0.00315	0.077
0.05824	2.4063	0.1423	2.444	1.49479	2.23439	0.00374	0.064
0.07949	2.4550	0.1916	2.411	1.49505	2.23519	0.00454	0.057
0.09879	2.4988	0.2348	2.378	1.49545	2.23636	0.00571	0.058

$(\Delta\epsilon/W)_{W \rightarrow 0} = 2.558$ $(\Delta n^2/W)_{W \rightarrow 0} = 0.085$
 $P_d = 65.8$ c.c. $\mu = 1.81$ D.

TABLE III
p-Chloro ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n_{12}^2	Δn^2	$\Delta n^2/W$
0.03126	2.3581	0.0941	2.926	1.49429	2.23292	0.00227	0.071
0.04401	2.3840	0.1200	0.728	1.49434	2.23306	0.00241	0.055
0.05876	2.4187	0.1547	2.632	1.49444	2.23322	0.00267	0.045
0.07459	2.4516	0.1876	2.516	1.49468	2.23398	0.00333	0.044
0.09454	2.4943	0.2303	2.437	1.49508	2.23528	0.00463	0.043

$(\Delta\epsilon/W)_{W \rightarrow 0} = 3.10$ $(\Delta n^2/W)_{W \rightarrow 0} = 0.080$
 $P_d = 80.4$ c.c. $\mu = 2.00$ D.

TABLE IV
o-Bromo ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.02250	2.3184	0.0544	2.419	1.49419	2.23261	0.00196	0.087
0.03968	2.3604	0.0964	2.429	1.49451	2.23368	0.00303	0.076
0.05608	2.3977	0.1337	2.384	1.49523	2.23571	0.00506	0.090
0.07352	2.4360	0.1720	2.339	1.49553	2.23667	0.00602	0.082
0.09053	2.4725	0.2085	2.303	1.49605	2.23815	0.00750	0.083
0.10760	2.5075	0.2435	2.261	1.49682	2.24047	0.00982	0.091

$$P_d = 85.5 \text{ c.c.} \quad \mu = 2.06 \text{ D.}$$

TABLE V
m-Bromo ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.01260	2.2945	0.0305	2.423	1.49383	2.23158	0.0093	0.074
0.02231	2.3179	0.0539	2.415	1.49417	2.23250	0.00185	0.083
0.02925	2.3333	0.0693	2.370	1.49450	2.23353	0.00288	0.098
0.04887	2.3793	0.1153	2.360	1.49499	2.23500	0.00435	0.089
0.06322	2.4104	0.1464	2.316	1.49555	2.23666	0.00601	0.095
0.08221	2.4512	0.1872	2.277	1.49591	2.23776	0.00711	0.087
0.10140	2.4908	0.2268	2.236	1.49663	2.23990	0.00925	0.091

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 2.454 \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.081$$

$$P_d = 83.1 \text{ c.c.} \quad \mu = 2.03 \text{ D.}$$

TABLE VI
p-Bromo ethylbenzene

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.02113	2.3190	0.0550	2.602	1.49458	2.23376	0.00311	0.147
0.03375	2.3642	0.0822	2.435	1.49499	2.23511	0.00446	0.132
0.04981	2.3802	0.1162	2.333	1.49571	2.23715	0.00650	0.131
0.06814	2.4194	0.1554	2.281	1.49637	2.23912	0.00847	0.124
0.09239	2.4706	0.2066	2.238	1.49707	2.24122	0.01057	0.114
0.12450	2.5421	0.2781	2.236	1.49783	2.24350	0.01285	0.103

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 2.640 \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.151$$

$$P_d = 87.2 \text{ c.c.} \quad \mu = 2.08 \text{ D.}$$

TABLE VII

Molecule	Calculated		Observed
	Vector	S & H	
<i>o</i> -Chloro ethyl benzene	1.36	1.79	1.57
<i>m</i> -Chloro ethyl benzene	1.91	2.01	1.81
<i>p</i> -Chloro ethyl benzene	2.13	2.23	2.00
<i>o</i> -Bromo ethyl benzene	1.31	2.01	2.06
<i>m</i> -Bromo ethyl benzene	1.86	1.99	2.03
<i>p</i> -Bromo ethyl benzene	2.08	2.18	2.08

Table VII shows that there is considerable amount of disagreement between the calculated and observed values. Even when inductive effects are considered the disagreement exists; in fact, the values calculated by simple vectorial method are better, in particular as we go to meta and para-chloro ethyl benzenes. It indicates that the induced effects are slight. The disagreement between the calculated and the observed values may be attributed to the assumed group moment of 0.58 for C_2H_5 which may be rather high. Unfortunately, there is no solution value available for ethyl benzene. A comparison with the corresponding chlorotoluene values reveals that the calculated values are 0.22 to 0.28 higher for the chloroethyl benzenes. The slight induced effects present in chloroethyl benzenes may be due to the higher polarisability of the ethyl group.

In the absence of induced and resonance effects, the chloro and bromo ethyl benzenes should have almost the same dipole moment as the corresponding substituted toluenes. It is also reasonable to expect slightly higher values for ethyl compounds owing to the slightly larger dipole moment and polarisability of the ethyl group. Examination of Table VIII (which gives the comparative data) indicates that the experimentally observed values for ethyl benzenes support the expectations.

TABLE VIII

	Ortho		Meta		Para	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
Chlorotoluene*	1.41	1.43	1.79	1.77	1.95	1.94
Chloro ethyl benzene	1.79	1.57	2.01	1.81	2.23	2.00
Bromotoluene*	1.38	1.44	1.76	1.75	1.92	1.93
Bromo ethyl benzene	2.01	2.06	1.99	2.03	2.18	2.08

* Moore and Hobbs (1948)

The agreement between the observed and calculated values of chloro and bromo toluenes, the fact that chloromesitylene has the same moment 1.55 as chlorobenzene while bromomesitylene and bromodurene have moments 1.52 and 1.55 respectively as compared to 1.50 for bromobenzene and that chloro ethyl benzenes have approximately same values as the corresponding toluenes show that effects of the methyl and ethyl groups upon the structures contributing to the moments of chloro and bromo benzenes as well as the inductive effect between the halogen and the adjacent methyl or ethyl groups are too small to be detected in the moments (Smyth and Lewis, 1940).

In the case of bromoethyl benzenes there is little variation in observed moment values from ortho- to para- position which is unexpected since for the corresponding bromotoluenes there is a definite increase of moment from ortho- to para-substitution. It is also interesting to note that while the calculated values by vector method show the increase from ortho- to para-substitution, the Smallwood and Herzfeld method does not give values with any definite indication of increase from ortho- to para- positions. The experimental observations were taken on two different samples obtained at different times but the same values of dipole moments for the three bromo ethyl benzenes were obtained. It is felt that further determinations on dipole moments should be carried out on other poly-substituted benzenes containing the ethyl group before attempting an explanation of the observed moments.

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REFERENCES

- Baker, J. W., and Groves, L. G., 1939, *Jour. Chem. Soc.*, 1144.
Moore, E. M., and Hobbs, M. E., 1949, *Jour. Am. Chem. Soc.*, 71, 411.
Murty, C. R. K., 1957, *Ind. J. Phys.*, 31, 256.
Smyth, C. P., and Lewis, G. L., 1940, *Jour. Am. Chem. Soc.*, 62, 721.