

DIPOLE MOMENTS OF SOME SUBSTITUTED
BENZENES AND PYRIDINES

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ABSTRACT. The dipole moments of seven substituted pyridines have been determined in dilute solution in benzene. The moment values are also calculated using group moments and vectorial method. The differences in moments between the calculated and observed values have been discussed.

INTRODUCTION

Since the publication of the electron diffraction results on pyridine by Schomaker and Pauling (1939), considerable interest was shown on the investigation of the dipole moments of these compounds. The electron diffraction studies have revealed that pyridine has a structure similar to that of benzene. The determination of the dipole moments of γ -substituted pyridines by Leiss and Curran (1945) has confirmed the similarity between the benzene and pyridine rings. To determine whether or not the carbon nitrogen linkage can be adequately represented by a single constant in heterocyclic ring systems, Schneider (1948) has determined the dipole moments of diazines and drawn the following conclusions: (1) the carbon nitrogen electric moment apparently has a constant value in the heterocyclic compounds investigated, (2) a heterocyclic ring of the pyridine type can be represented by a plane hexagon and (3) in the compounds investigated, all bonds between nitrogen and carbon seem to be electrically equivalent so far as dipolar characteristics are concerned.

The present investigation on substituted pyridines has been undertaken primarily to obtain dipole moment data on as many pyridine compounds as possible in order to understand their structure.

The experimental arrangement used for measurement of dielectric constant and refractive index of solutions and the method of calculation of dipole moments from the experimental observations had been described previously by the author (1957). All the substituted pyridines were supplied by L. Lights and Co., England and were reported to be of a high standard of purity. The solvent benzene was also of A.R. grade of purity.

CALCULATION OF μ FROM GROUP MOMENTS

For the calculation of dipole moment in the case of 2- and 3-acetyl pyridines, group moments of 2.22 and 2.89 have been assumed for N- and acetyl

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groups respectively. It has also been assumed that the acetyl group moment makes an angle of 55° with the C-C bond to the ring (Smyth, 1955). This value of the angle has been obtained from the dipole moment of *p*-diacetyl benzene.

In the case of amino methyl pyridines, the group moments 0.40 and 1.53 have been assumed for CH_3 and NH_2 . It is also assumed that the moment of NH_2 acts along the C-C bond to the ring following the example of other substituted pyridines investigated by Curran (1945). If it is assumed that NH_2 group moment makes an angle of 38° with the C-C bond following the example of substituted anilines, the calculated values are very much different from the observed values.

RESULTS AND DISCUSSION

Dipole moments of seven substituted pyridines have been determined and the results are given in Tables I to VII. The observed and calculated values of dipole moments are given in Table VIII.

TABLE I
2-Acetyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0 01204	2.3639	0.0099	8 200	1.49416	2 23252	0.00187	0.155
0 02223	2.4398	0 1758	7 911	1 49432	2 23289	0 00224	0.101
0 03479	2 5335	0.2695	7.745	1.49454	2.23364	0.00299	0.086
0 04851	2 6360	0 3720	7.670	1.49454	2 23364	0.00299	0.062
0.06299	2.7448	0 4808	7.632	1.49459	2 23381	0.00316	0.050
0.07645	2.8489	0 5849	7.650	1.49474	2.23425	0.00360	0.047

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 8.08, \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.124, \quad P_d = 163.4 \text{ c.c.}, \quad \mu = 2.85\text{D}$$

TABLE II
3-Acetyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.02276	2.4109	0.1469	6.455	1.49522	2.23569	0 00504	0.221
0.03499	2.4829	0.2189	6.253	1.49577	2.23733	0.00668	0.191
0.04908	2.5722	0.3082	6.280	1.49598	2.23795	0.00730	0.149
0.06272	2.6550	0.3910	6.234	1.49633	2 23901	0.00836	0.433
0.07352	2.7247	0.4607	6.266	1.49668	2.24007	0.00942	0.128

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 6.48, \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.262, \quad P_d = 128.6 \text{ c.c.}, \quad \mu = 2.53\text{D}$$

TABLE III
2-Amino-3-methyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.00263	2.2776	0.0136	5.190	1.49383	2.23154	0.00089	0.383
0.00448	2.2880	0.0240	5.348	1.49399	2.23202	0.00137	0.306
0.00856	2.3125	0.0485	5.665	1.49421	2.23267	0.00202	0.236
0.01417	2.3477	0.0837	5.912	1.49467	2.23404	0.00339	0.239
0.01820	2.3726	0.1086	5.971	1.49473	2.23423	0.00358	0.197

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 5.08, \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.342, \quad P_d = 94.9 \text{ c.c.}, \quad \mu = 2.17 \text{ D}$$

TABLE IV
2-Amino-4-methyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.00207	2.2843	0.0203	9.766	1.49386	2.23163	0.00098	0.473
0.00436	2.2987	0.0347	7.943	1.49414	2.23246	0.00181	0.415
0.00721	2.3179	0.0539	7.482	1.49419	2.23261	0.00196	0.272
0.01021	2.3353	0.0713	6.984	1.49444	2.23335	0.00270	0.264
0.01267	2.3438	0.0798	6.306	1.49464	2.23396	0.00331	0.261

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 8.67, \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.550, \quad P_d = 141.0 \text{ c.c.}, \quad \mu = 2.65 \text{ D}$$

TABLE V
2-Amino-5-methyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/W$
0.00202	2.2782	0.0142	7.021	1.49411	2.23237	0.00172	0.851
0.00294	2.2819	0.0179	6.103	1.49427	2.23284	0.00219	0.747
0.00678	2.3026	0.0386	5.689	1.49462	2.23390	0.00325	0.479
0.00993	2.3181	0.0541	5.450	1.49462	2.23390	0.00325	0.327
0.01371	2.3353	0.0713	5.198	1.49464	2.23396	0.00331	0.241

$$(\Delta\epsilon/W)_{W \rightarrow 0} = 6.32, \quad (\Delta n^2/W)_{W \rightarrow 0} = 0.880, \quad P_d = 111.4 \text{ c.c.}, \quad \mu = 2.85 \text{ D}$$

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TABLE VI
2-Amino-6-methyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n_{12}^2	Δn^2	$\Delta n^2/W$
0.01405	2.3157	0.0517	3.678	1.49561	2.23686	0.00621	0.442
0.01890	2.3348	0.0708	3.729	1.49633	2.23900	0.00835	0.440
0.02816	2.3699	0.1050	3.761	1.49692	2.24078	0.01013	0.300
0.03601	2.4023	0.1383	3.840	1.49756	2.24269	0.01204	0.334
0.04561	2.4400	0.1760	3.859	1.49783	2.24350	0.01285	0.282

$(\Delta\epsilon/W)_{W \rightarrow 0} = 3.605$, $(\Delta n^2/W)_{W \rightarrow 0} = 0.510$, $P_d = 63$ e.o., $\mu = 1.77$ D

TABLE VII
2-Amino-4-6-dimethyl pyridine

W	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/W$	n_{12}	n_{12}^2	Δn^2	$\Delta n^2/W$
0.01112	2.3138	0.0498	4.483	1.49528	2.23586	0.00521	0.400
0.01738	2.3389	0.0740	4.308	1.49587	2.23703	0.00698	0.402
0.02518	2.3664	0.1024	4.069	1.49629	2.23890	0.00825	0.328
0.03487	2.3999	0.1359	3.896	1.49668	2.24007	0.00942	0.270
0.04056	2.4133	0.1493	3.696	1.49747	2.24242	0.01177	0.290

$(\Delta\epsilon/W)_{W \rightarrow 0} = 4.72$, $(\Delta n^2/W)_{W \rightarrow 0} = 0.520$, $P = 97.7$ e.o., $\mu = 2.20$ D

TABLE VIII

Substance	μ observed	μ calculated
2-Acetyl pyridine	2.85	2.81 D
3-Acetyl pyridine	2.53	0.71
2-Amino-3-methyl pyridine	2.17	2.35
2-Amino-4-methyl pyridine	2.65	2.28
2-Amino-5-methyl pyridine	2.35	1.92
2-Amino-6-methyl pyridine	1.77	1.59
2-Amino-4 : 6-dimethyl pyridine	2.20	1.92

In the case of acetyl pyridines, the agreement between calculated and observed values is satisfactory when the acetyl group is in the α -position. For β -acetyl

pyridine the calculated value is very low compared to the observed value of 2.53. This difference is so much that it cannot be accounted for by experimental errors. The discrepancy may be understood when the γ -acetyl pyridine is also investigated.

The group moments of CH_3 and NH_2 have the same sign but opposite to that of pyridine moment. As the group NH_2 is fixed in the α -position in all the compounds investigated, the moment to be expected for 2-amino-3-methyl pyridine is that of 2-amino pyridine plus the small contribution of CH_3 . The observed value appears to be somewhat less than the expected value. When CH_3 is in the γ -position the moment observed is maximum indicating negligible effect of NH_2 on CH_3 and an approximate moment of $2.17 + 0.40 = 2.57$ may be expected for this compound. The observed value of 2.65 shows fair agreement with the expected value though considerably greater than the calculated value obtained by simple vectorial method. The value of 2.17 for 2-amino pyridine includes the inductive and resonance effects between pyridine and NH_2 group.

In the case of 2-amino-5-methyl pyridine the CH_3 group is in the meta-position relative to N- and away from NH_2 unlike in 2-amino-3-methyl pyridine. Assuming negligible effect of NH_2 , a moment of 2.39 is to be expected which is close to 2.35 observed for this compound. 2-amino-6-methyl pyridine should have the minimum moment since both NH_2 and CH_3 are ortho-to N. The observed value of 1.77 is minimum for all these compounds and is slightly greater than the value of 1.65 observed for 2 : 6-dimethyl pyridine as is to be expected.

The moment value for 2-amino-4-6-dimethyl pyridine should be obtained by adding CH_3 group moment to that of 2-amino-6-methyl pyridine since CH_3 which is added is para-to N. The observed value of 2.20 is in reasonable agreement with 2.17 which is the expected value.

In conclusion, the author considers that a much larger amount of data on pyridine compounds with various substitutions in different positions have to be collected before the structure and resonance effects in these compounds can be completely discussed.

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