The Effect of *Ortho*-Substitution on the Dipole Moments of Aniline Derivatives *

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According to a suggestion by Docent N. Löfgren, Stockholm, a systematic investigation of the dipole moments of toluidines and xylidines may throw light on the special effect of substituents in the *ortho*-position, which is usually called the *ortho*-effect.

The present study includes the determination of the electric moments of some derivatives of aniline, in which one or more methyl groups are substituted at different positions in the benzene nucleus as well as at the nitrogen atom. Though some of the dipole moments now reported have been measured before by other authors we thought it advisable to measure the moments of all the substances concerned with the same apparatus and in the same solvent in order to obtain strictly comparable values. It should not be taken for certain that the new values — taken as absolute data — are more accurate than those obtained earlier, but it is assumed that the new measurements are more consistent among themselves.

PREPARATIONS

Benzene. A thiophene-free product from Baker's Ltd. was stored over sodium wire for three months. It was distilled over sodium in an atmosphere of dry nitrogen immediately before use.

Aniline. The purest Merck product was treated according to the method described by Timmermans and Hennaut-Rolland [1]. The final distillation under reduced pressure, in this as well as in all the following cases, was performed in a stream of dry nitrogen. B. p. 71° (11 mm).

N-Methyl aniline. The best commercial product was purified by conversion into the nitrosoamine. This was reduced by stannous chloride in a manner similar to that recommended by Blatt [2] for the synthesis of N-ethyl *m*-toluidine. At the final distillation the b. p. was 84° (13 mm).

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N,N-Dimethyl aniline. The technical product was steam-distilled, fractionally crystallised, and distilled twice under reduced pressure. B. p. 78° (12 mm).

Ortho-Toluidine. The purest Merck product was fractionally distilled at atmospheric pressure. The slightly yellow fraction boiling at 194° (uncorr.) was collected and redistilled. B. p. 84° (11 mm).

N-Methyl o-toluidine. This substance was prepared from the purified o-toluidine by Blatt's method [2]. B. p. 89° (11 mm).

N,N-Dimethyl o-toluidine. The methylation was performed with methyl iodide in alkaline solution in accordance with the method described by Noelting [3] for the synthesis of N,N-dimethyl 3,5-xylidine. The substance boiled at 74° (14 mm).

Meta-Toluidine. The purest commercial product was fractionally distilled at atmospheric pressure. The fraction boiling at 197° (uncorr.) was collected and redistilled under reduced pressure. B. p. 87° (11 mm).

N-Methyl m-toluidine. The substance was prepared in a similar manner to the corresponding o-compound. B. p. 97° (14 mm).

N,N-Dimethyl m-toluidine. The same method of preparation was used as in the case of the corresponding o-compound. B. p. 85° (9 mm).

Para-Toluidine. The best Merck product was purified by three recrystallisations from ligroin. M. p. 46 — 47°.

N-Methyl p-toluidine. The substance was synthesised from the formyl compound by the method described by Bamberger and Wulz [4]. B. p. 94° (14 mm).

N,N-Dimethyl p-toluidine. Noelting's method of preparation [3] was used. The boiling point was 90° (13 mm).

2,4-Xylidine. A pure Eastman Kodak Co. product was fractionally distilled at atmospheric pressure. The slightly yellow fraction boiling at 210° (uncorr.) was collected. After redistillation the product was almost uncoloured. B. p. 96° (12 mm).

N-Methyl 2,4-xylidine. The substance was synthesised by Blatt's method [2]. B. p. 103° (12 mm).

N,N-Dimethyl 2,4-xylidine. The preparation was carried out in the way described by Noelting [3]. B. p. 87° (13 mm).

2,6-Xylidine. A commercial product was purified by treatment with conc. sulphuric acid, ether extraction and repeated fractional distillation. B. p. 96° (12 mm).

N-Methyl 2,6-xylidine. The acetyl derivative of the primary amine was methylated with methyl iodide and converted into the nitrosoamine as described by Friedländer [5]. The nitrosoamine was then treated according to Blatt [2]. The boiling point of the final product was 87° (13 mm).

N,N-Dimethyl 2,6-xylidine. The substance was synthesised by the method of Fischer and Windaus [6]. B. p. 74° (11 mm).

METHOD AND APPARATUS

The dielectric constants and the specific volumes of dilute benzene solutions of the substances were measured at 25° ± 0.05°. In order to prepare a solution the substance was distilled into a weighing glass with ground-glass stopper and weighed, care being taken to avoid moisture. Then, benzene was added from a syringe and weighed. The same solution was used for measurements of both dielectric constant and specific volume.

The specific volumes were determined with Ostwald-Sprengel pycnometers fitted with carefully ground caps. They had a volume approximately equal to 5 cm^3.

The dielectric constants were measured with an alternating-current heterodyne beat apparatus built in this laboratory according to a design published by Hudson and Hobbs [7]. The fundamental frequency of the crystal controlled oscillator was 1 000 kilocycles. In the measuring circuit the frequency could be adjusted either to 1 000 kilocycles or to the first harmonic of the crystal, 2 000 kilocycles, by using different coils. The first harmonic was used for the present measurements. The beat frequency was adjusted to the frequency of the alternating-current, 50 cycles. The two points at each side of the zero beat frequency were determined with aid of a loud speaker and a cathode ray tube.

The measuring condenser was a modification of one described by Arrhenius [8]. The solution was placed in a cup of silver, which formed one part of the condenser. The other part was a plate of pure silver, which could be fixed at different distances from the bottom of the cup varying between 0.5 and 2 mm. The cup was filled with 5.0 cm^3 of the solution. The maximum difference in air capacity between two settings was 2 $\mu\mu$f. The variable capacity of the measuring condenser, and thus its volume, was kept small in order to make it possible to carry out a determination of the dipole moment with about 5 g of a substance, or even less. By measuring the difference between two settings instead of the total capacity of the condenser, inaccuracies due to the connections between the measuring cell and the main part of the oscillator were without influence on the capacity determination.

Two variable cylinder condensers were connected in parallel with the measuring condenser, the larger having a minimum capacity of 125 $\mu\mu$f and a variable capacity of 350 $\mu\mu$f, and the smaller a minimum capacity of 20 $\mu\mu$f and a variable capacity of 11 $\mu\mu$f. The inner cylinder of the smaller condenser could be moved with aid of a screw, each revolution allowing a movement of 0.5 mm. One revolution corresponded to a capacity change of 0.1 $\mu\mu$f and a reading could be made to 0.005 revolution, i. e. 0.0005 $\mu\mu$f. However, this degree of accuracy is not significant. The mechanical deficiency of the condenser made it necessary to take several readings for each complete measurement, usually eight to ten. These readings did not agree to more than 0.005 $\mu\mu$f. As the capacity changes were about 5 $\mu\mu$f the accuracy of the dielectric constant measurement would be 0.1 %. The cylinder condenser was calibrated in units of the measuring condenser. Thus, the accuracy quoted above referred to relative capacity values. In order to obtain "absolute" values we assigned to our benzene sample the value of the dielectric constant given by Hartshorn

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Table 1. Measurements on benzene solutions at 25° C. The values given for the pure solvent are extrapolated ones.

$f_2 \cdot 10^5$	ε	v	$f_2 \cdot 10^5$	ε	v
	Aniline			Methyl aniline	
0	2.2686	1.14457	0	2.2665	1.14445
983	2.3089	1.14268	1225	2.3259	1.14239
1417	2.3206	1.14164	2627	2.3884	1.14007
1782	2.3323	1.14092	3030	2.4042	1.13907
3073	2.3859	1.13841	5325	2.5076	1.13539
	Dimethyl aniline			*Ortho*-Toluidine	
0	2.2723	1.14456	0	2.2815	1.14478
660	2.2938	1.14366	1722	2.3475	1.14143
1842	2.3402	1.14217	2733	2.3848	1.13927
2504	2.3594	1.14116	3403	2.4153	1.13813
4152	2.4175	1.13897	4304	2.4453	1.13629
	Methyl *o*-toluidine			Dimethyl *o*-toluidine	
0	2.2751	1.14455	0	2.2711	1.14452
482	2.2995	1.14369	1282	2.2852	1.14332
991	2.3206	1.14274	1974	2.2931	1.14259
1694	2.3495	1.14153	2496	2.3009	1.14199
2293	2.3851	1.14041	3413	2.3102	1.14118
			3851	2.3141	1.14081
	Meta-Toluidine			Methyl *m*-toluidine	
0	2.2696	1.14425	0	2.2770	1.14460
1368	2.3144	1.14247	1014	2.3140	1.14299
2165	2.3399	1.14131	1869	2.3443	1.14163
3150	2.3688	1.14014	2772	2.3844	1.14016
4004	2.4005	1.13882	3435	2.4005	1.13916
	Dimethyl *m*-toluidine			*Para*-Toluidine	
0	2.2680	1.14468	0	2.2726	1.14454
726	2.2942	1.14375	1347	2.3090	1.14228
1338	2.3126	1.14304	1406	2.3140	1.14211
1387	2.3096	1.14296	2455	2.3396	1.14036
1995	2.3390	1.14213	3608	2.3742	1.13840
2393	2.3495	1.14164			
2792	2.3640	1.14118			
2838	2.3595	1.14115			

Table 1. (cont.)

$f_2 \cdot 10^5$	ε	v	$f_2 \cdot 10^5$	ε	v
	Methyl p-toluidine			Dimethyl p-toluidine	
0	2.2742	1.14458	0	2.2650	1.14446
994	2.3057	1.14299	1666	2.3082	1.14259
1913	2.3272	1.14148	2667	2.3273	1.14141
2432	2.3468	1.14068	3233	2.3430	1.14076
3612	2.3820	1.13877	4281	2.3723	1.13962
	2,4-Xylidine			Methyl 2,4-xylidine	
0	2.2727	1.14439	0	2.2686	1.14461
876	2.2989	1.14306	818	2.2990	1.14331
1965	2.3306	1.14137	1382	2.3149	1.14248
2289	2.3359	1.14070	2219	2.3452	1.14105
3003	2.3618	1.13963	3146	2.3794	1.13963
	Dimethyl 2,4-xylidine			2,6-Xylidine	
0	2.2729	1.14456	0	2.2774	1.14449
1276	2.2828	1.14371	597	2.3004	1.14346
1973	2.2872	1.14302	1502	2.3380	1.14169
2806	2.2922	1.14258	1681	2.3396	1.14151
3503	2.2995	1.14204	2273	2.3678	1.14046
			3084	2.3943	1.13892
			3150	2.3998	1.13873
			4947	2.4698	1.13562
	Methyl 2,6-xylidine			Dimethyl 2,6-xylidine	
0	2.2749	1.14452	0	2.2697	1.14458
1086	2.3018	1.14296	1359	2.2868	1.14374
1673	2.3160	1.14220	1549	2.2883	1.14358
2785	2.3380	1.14044	2148	2.2947	1.14326
4785	2.3908	1.13772	2913	2.3055	1.14274

and Oliver [9], $\varepsilon_{25°} = 2.2725$, which is in good agreement with the value obtained more recently by van der Maesen [10], $\varepsilon_{25°} = 2.2738$.

The results obtainable directly from the measurements were the dielectric constant, ε, and the specific volume, v, of the solutions. The plot of ε as well as that of v against the mole fraction of the solute, f_2, gave straight lines. The slopes, $\partial\varepsilon/\partial f_2$ and $\partial v/\partial f_2$, and the intercepts at $f_2 = 0$, ε_1 and v_1, were calculated by the method of least squares. The polarisation of the solute at infinite dilu-

Table 2. Calculated values of polarisations and dipole moments.

Substance	$\dfrac{\partial \varepsilon}{\partial f_2}$	$-\dfrac{\partial v}{\partial f_2}$	P_2^0 cm^3	MR_D cm^3	μ D
Aniline	3.77	0.202	82.4 $\pm$ 3.6	30.58 [12]	1.59 $\pm$ 0.03
Methyl aniline	4.56	0.171	99.6 1.7	35.69 [1]	1.77 .02
Dimethyl aniline	3.51	0.134	89.9 0.8	40.85 [15]	1.55 .01
o-Toluidine	3.84	0.197	88.3 2.2	34.98 [13]	1.61 .02
Methyl o-toluidine ..	4.66	0.180	105.5 4.5	40.43	1.78 .04
Dimethyl o-toluidine ..	1.14	0.098	60.5 0.8	44.62 [14]	0.88 .01
m-Toluidine	3.23	0.133	80.9 1.7	35.29 [13]	1.49 .02
Methyl m-toluidine ..	3.69	0.159	91.8 3.6	40.60	1.58 .03
Dimethyl m-toluidine..	3.36	0.125	92.5 2.7	45.68 [14]	1.51 .02
p-Toluidine	2.80	0.170	73.7 1.8	35.91 [13]	1.36 .02
Methyl p-toluidine ..	2.96	0.161	81.0 2.4	40.67	1.41 .02
Dimethyl p-toluidine ..	2.47	0.114	79.7 2.7	45.68 [14]	1.29 .02
2,4-Xylidine	2.91	0.158	80.3 3.1	40.08 [15]	1.40 .03
Methyl 2,4-xylidine ..	3.49	0.158	93.7 1.7	45.25	1.54 .02
Dimethyl 2,4-xylidine .	0.73	0.072	60.0 0.4	49.55 [15]	0.71 .01
2,6-Xylidine	3.88	0.180	94.0 1.1	39.94 [15]	1.63 .02
Methyl 2,6-xylidine ..	2.39	0.143	77.9 1.6	44.46	1.28 .01
Dimethyl 2,6-xylidine .	1.21	0.063	67.1 1.2	48.99 [15]	0.94 .01

tion, P_2^0, was calculated from the equation derived by Halverstadt and Kumler [11]:

$$P_2^0 = \frac{3\,\dfrac{\partial \varepsilon}{\partial f_2}\,v_1 M_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\left[M_2 v_1 + M_1\,\frac{\partial v}{\partial f_2}\right]$$

The sum of the electronic and the atomic polarisations was set equal to the molar refraction of the sodium line, MR_D. In cases when the value of MR_D is not known the refractive index of the pure substance was determined with an Abbe refractometer, and the density of the substance was measured with a pycnometer of volume approximately equal to 1 cm^3. As an uncertainty in this determination is not very important, an accuracy in MR_D greater than 0.1 % was not attempted. Finally, the dipole moment, μ, was calculated from:

$$\mu = 0.22118 \, \sqrt{P_2^0 - MR_D} \qquad \text{Debye } (D)$$

where $0.22118 \cdot 10^{-18}$ is the value of $\sqrt{4\pi N/9kT}$ at $T = 298°\ K$.

Table 3. Previously published dipole moments obtained from measurements on benzene solutions.

Substance	Dipole moment	
	This paper	Previous investigations
Aniline	1.59	1.55, [16] 1.52, [17] 1.51 [18]
Methyl aniline	1.77	1.64 [19]
Dimethyl aniline	1.55	1.58, [19, 20] 1.55 [21]
o-Toluidine	1.61	1.58, [17] 1.65 [22]
m-Toluidine	1.49	1.44, [17] 1.51 [22]
p-Toluidine	1.36	1.31, [17] 1.36 [22]
Dimethyl p-toluidine	1.29	1.29 [20]

RESULTS

The data of the measurements of dielectric constants and specific volumes are collected in Table 1. Table 2 contains the computed values of the slopes of the extrapolation curves, of the polarisations, and of the dipole moments.

As is seen from Table 3 the agreement between the above results and values obtained previously for dipole moments is fairly good. Table 4 shows the differences between the moments of primary, secondary, and tertiary amines.

Table 4.

Primary amine	Difference between the moments of:		
	sec. — prim.	tert. — sec.	tert. — prim.
Aniline	+ 0.18	− 0.22	− 0.04
m-Toluidine	+ 0.09	− 0.07	+ 0.02
p-Toluidine	+ 0.05	− 0.12	− 0.07
o-Toluidine	+ 0.17	− 0.90	− 0.73
2,4-Xylidine	+ 0.14	− 0.83	− 0.69
2,6-Xylidine	− 0.35	− 0.34	− 0.69

DISCUSSION

The dipole moments of the primary amines show that *ortho* substitution changes the moment less than does *meta* or *para* substitution. Thus, the dipole moment of o-toluidine is only 0.02 *D* larger than the moment of aniline, and

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the moment of 2,4-xylidine is 0.04 D larger than that of p-toluidine. This small change of the moment is certainly the result of opposing effects, namely the finite moment of the methyl group, which tends to increase the resulting moment, and contrary moments due to induction, cf. Smallwood and Herzfeld [23]. Perhaps a change of valence angles is also involved.

The substitution of one methyl group at the nitrogen atom in most cases increases the resulting moment by 0.1—0.2 D. The only exception is 2,6-xylidine, where there are two methyl groups in the o-position to the amino group. In this case the resulting moment is 1.28 D, which is 0.35 D *smaller* than the moment of the primary amine. Moreover, the moment is only 0.1 D larger than that of a secondary aliphatic amine, dimethyl amine, which has a dipole moment of 1.17 D calculated from measurements on benzene solutions [24].

All the moments of the tertiary aniline homologues are smaller than those of the corresponding secondary amines. It is noteworthy that the substitution of *one* methyl group at the nitrogen atom *increases* the resulting moment, whereas the substitution of *two* methyl groups *reduces* the moment. When the molecules in question do not possess a methyl group in the o-position the moments of the tertiary amines deviate by only about 0.05 D from the moments of the primary amines. However, when the tertiary amine has one or two methyl groups in the o-position its dipole moment is 0.7 D smaller than the moment of the primary amine, cf. Table 4. The dipole moment of these tertiary aniline homologues have almost the same value as those of aliphatic tertiary amines, namely 0.86 D when measured in benzene solution [24].

To sum up: three or four methyl groups in the proximity of the nitrogen atom of aniline, that is substituted either at the nitrogen atom or in the o-position, twist the amino group around the carbon-nitrogen bond, so that one of the atoms, or groups, attached to the nitrogen lies above, and the other below, the plane of the benzene ring. This causes a change of the dipole moment from the value typical of an aromatic amine to that typical of an aliphatic amine. It has earlier been pointed out by Hampson and coworkers [25] that four methyl groups in the proximity of the nitrogen inhibit the resonance of the molecule.

It is interesting to note that the inhibition of resonance is also manifest in the ultra-violet absorption spectra of *ortho*-substituted derivatives of dimethyl aniline [26], as well as in the value of the atomic refractivity of the nitrogen of dimethyl 2,6-xylidine, calculated by Thomson [15]. This author has also measured the basic strengths of homologues of dimethyl aniline [27] and has found a clear difference between molecules with and without inhibited resonance.

SUMMARY

1. The dipole moments of 18 aniline homologues have been measured in benzene solutions at 25° C.

2. When the *ortho*-effect is not involved, the secondary amine has a larger moment than the primary one, and the tertiary amine has a smaller moment than the secondary one.

3. Three or four methyl groups in the proximity of the nitrogen atom change the moment from the value typical of an aromatic amine to that typical of an aliphatic one.

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