

DIPOLE MOMENTS OF SOME ALIPHATIC AMINES

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ABSTRACT. The dipole moments of eight higher members of the aliphatic amines have been determined in solution in benzene at 30°C and the results are discussed in the light of their molecular structure. Apart from the fact that the reported values of the dipole moments are new, the investigation was undertaken as a complementary to measurements on the same molecules in the centimetric region.

INTRODUCTION

The apparent polarisations of ammonia and its mono-, di-, tri- methyl and ethyl derivatives have been studied in the solvent benzene by Le Fevre and Russell (1947) and Barclay, Le Fevre and Smythe (1950). The latter authors have also extended the investigations (1951) to *n*-propyl and *n*-butyl amines for which the variation of moment with state is studied and also the apparent moments in solution of certain other amines. A positive solvent effect is noted by all these investigators. From a study of the moments of eighteen aliphatic and aromatic amines in seven non-polar solvents and of fifteen liquid amines in the pure state, Cowley (1952) could show that in most cases the solvent effect is small. The solvents benzene, toluene and dioxane gave small positive solvent effects confirming the previous results but with other solvents a small negative solvent effect is the more usual observation. Variation of polarisation with change of concentration from infinite dilution to the pure solute is also studied and is shown to depend on the type of amine and also on the value of its dielectric constant. The dipole moment values are corrected for the atom polarisation which is assumed as 5 per cent of the electron polarisation.

The aliphatic amines may be considered as substitution products of ammonia in which one hydrogen atom is replaced by an alkyl group. The bond angle of ammonia (109°) may be taken as evidence of the existence of hybridized orbitals. It has been found that the lone-pair contribution to the resultant moment is much higher than in the case of water. Arguments similar to those of ammonia also apply to the aliphatic amines. The low moment of tri-methylamine may be explained as due in part to the wider bond angle compared to that in ammonia, with the result that the lone-pair orbital has less *s*-character and hence makes a smaller contribution to the dipole moment.

Till now all observations are confined only up to butylamine. There are no investigations on the still higher aliphatic amines. A systematic study of eight higher members of the homologous series, starting from amylamine to decylamine, is made by the author, the measurements being carried out in solution in benzene at 30°C. Not only do the results serve as an extension of the previous work, they also provide a useful check on the values derived by the author from measurements made on the same molecules in the microwave region (to be published shortly).

EXPERIMENTAL

The experimental technique and the method of computing the moment from the observed data are described in an earlier publication of the author (1956).

RESULTS AND DISCUSSION

The detailed observations of dielectric constant and refractive index are presented in Tables I to VIII and the consolidated results are shown in Table IX. For completeness, literature values on the lower members of the series (Smith, 1955a) are also given in Table IX.

Let us assume a bond angle of 110° in methylamine, a set of reference axes with the N atom at the origin and fix the *x*-axis in the axis of symmetry (of the parent NH₃) and choose the *xy*-plane to pass through the C atom. The moment components outside the plane of symmetry cancel one another. The bond moments may be derived from the values for ammonia (1.45D) and trimethylamine (0.64 D) as

$$\begin{aligned} 3(\text{H}-\text{N}) \cos 68^\circ &= 1.45 & \text{H}-\text{N} &= 1.29 \\ 3(\text{R}-\text{N}) \cos 70^\circ &= 0.64 & \text{R}-\text{N} &= 0.62 & \text{C}-\text{N} &= 0.22 \end{aligned}$$

Using these values, we get for methylamine

$$\begin{aligned} m_x &= (\text{R}-\text{N}) \cos 70^\circ + 2(\text{H}-\text{N}) \cos 70^\circ = 1.09 \\ m_y &= -(\text{R}-\text{N}) \sin 70^\circ + 2(\text{H}-\text{N}) \sin 70^\circ \sin 30^\circ = -0.63 \\ \mu &= (m_x^2 + m_y^2)^{1/2} = 1.26. \end{aligned}$$

The calculated value thus agrees well with the gas value of 1.28. It may be shown that the angle between the molecular dipole axis and the C-N bond direction is 30° + 70° = 100° (Smyth, 1955). The calculated value for all the other higher amines (only one H atom of NH₃ is substituted) is the same as for methylamine, except for some induced effects of the primary dipole on the hydrocarbon chains. It is known that the dipole axis in methylamines is not far from perpendicular to the direction of maximum polarisability and hence the solvent effect causes the apparent moments in solution to be higher than the

TABLE I
n-Amylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.01635	2.3065	0.0425	2.600	1.49298	2.22900	0.00558	0.341
0.04442	2.3796	0.1156	2.603	1.48976	2.21939	0.01519	0.342
0.06269	2.4283	0.1643	2.620	1.48798	2.21409	0.02049	0.327
0.08900	2.4951	0.2311	2.596	1.48563	2.20681	0.02777	0.312
0.10210	2.5283	0.2643	2.589	1.48305	2.19945	0.03513	0.344
0.11950	2.5738	0.3098	2.593	1.48120	2.19395	0.04003	0.340
0.13090	2.5987	0.3347	2.557	1.47980	2.18981	0.04477	0.342

$A = (\Delta\epsilon/w)_w \rightarrow 0 = 2.605$ $P_0 = 48.61$ e.o.c.
 $B = (\Delta n^2/w)_w \rightarrow 0 = -0.330$ $\mu = 1.55 D$.

TABLE II
n-Hexylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.01931	2.3083	0.0443	2.292	1.49436	2.22798	0.00660	0.342
0.03386	2.3389	0.0749	2.211	1.49102	2.22312	0.01145	0.338
0.04774	2.3607	0.1027	2.150	1.48904	2.21902	0.01556	0.326
0.07396	2.4180	0.1540	2.082	1.48686	2.21076	0.02382	0.322
0.08950	2.4458	0.1818	2.031	1.48500	2.20522	0.02936	0.328
0.10280	2.4654	0.2014	1.959	1.48339	2.20045	0.03413	0.332

$A = 2.320$ $B = -0.331$ $P_0 = 50.81$ e.o.c. $\mu = 1.59 D$

TABLE III
n-Heptylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.01372	2.2916	0.0276	2.011	1.49325	2.22981	0.00477	0.348
0.02904	2.3231	0.0591	2.036	1.49158	2.22482	0.00976	0.336
0.04256	2.3483	0.0843	1.982	1.49003	2.22020	0.01438	0.338
0.06176	2.3837	0.1197	1.937	1.48810	2.21444	0.02014	0.326
0.07504	2.4069	0.1429	1.904	1.48678	2.21050	0.02408	0.321
0.09217	2.4374	0.1734	1.881	1.48467	2.20425	0.03033	0.325
0.10490	2.4510	0.1870	1.782	1.48340	2.20048	0.03410	0.325

$A = 2.040$ $B = -0.332$ $P_0 = 51.76$ e.o.c. $\mu = 1.60 D$.

TABLE IV
n-Octylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.00673	2.2732	0.0092	1.374	1.49423	2.23272	0.00186	0.276
0.01253	2.2809	0.0169	1.351	1.49364	2.23097	0.00361	0.288
0.02077	2.2920	0.0280	1.345	1.49292	2.22880	0.00578	0.278
0.03260	2.3070	0.0430	1.320	1.49182	2.22552	0.00906	0.278
0.05841	2.3386	0.0746	1.277	1.48791	2.21899	0.01559	0.267
0.09126	2.3768	0.1128	1.236	1.48702	2.21123	0.02335	0.256
0.11300	2.3926	0.1286	1.139	1.48525	2.20507	0.02861	0.253
$A = 1.380$	$B = -0.271$		$P_0 = 40.45$ c.c.		$\mu = 1.42 D.$		

TABLE V
n-Decylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.00615	2.2706	0.0066	1.078	1.49433	2.23301	0.00157	0.256
0.01369	2.2785	0.0145	1.057	1.49377	2.23135	0.00323	0.236
0.02216	2.2877	0.0237	1.070	1.49313	2.22944	0.00514	0.232
0.02956	2.2940	0.0300	1.014	1.49257	2.22777	0.00681	0.230
0.03749	2.3014	0.0374	0.997	1.49171	2.22520	0.00938	0.250
0.04500	2.3082	0.0442	0.983	1.49111	2.22342	0.01116	0.248
0.06039	2.3219	0.0579	0.059	1.48971	2.21925	0.01533	0.254
$A = 1.090$	$B = -0.244$		$P_0 = 39.77$ c.c.		$\mu = 1.41 D.$		

TABLE VI
Isoamylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	$\frac{\Delta n^2}{(-)}$	$\frac{\Delta n^2/w}{(-)}$
0.01242	2.2950	0.0310	2.494	1.49348	2.23048	0.00410	0.330
0.02973	2.3394	0.0754	2.536	1.49167	2.22507	0.00951	0.320
0.04033	2.3672	0.1032	2.560	1.49041	2.22132	0.01326	0.329
0.05860	2.4141	0.1501	2.562	1.48829	2.21501	0.01957	0.334
0.06960	2.4404	0.1764	2.535	1.48720	2.21175	0.02283	0.328
0.09185	2.4913	0.2273	2.475	1.48465	2.20418	0.03040	0.331
0.10550	2.5200	0.2560	2.426	1.48295	2.19913	0.03545	0.336
$A = 2.540$	$B = -0.330$		$P_0 = 47.40$ c.c.		$\mu = 1.53 D.$		

TABLE VII
Isohexylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	Δn^2 (-)	$\Delta n^2/w$ (-)
0.01114	2.2929	0.0289	2.592	1.49371	2.23117	0.00341	0.306
0.02810	2.3235	0.0595	2.575	1.49255	2.22770	0.00668	0.298
0.03402	2.3536	0.0896	2.632	1.49152	2.22464	0.00994	0.292
0.04381	2.3845	0.1205	2.751	1.49057	2.22179	0.01279	0.292
0.05331	2.4137	0.1497	2.809	1.48973	2.21928	0.01530	0.287
0.06032	2.4379	0.1739	2.883	1.48907	2.21733	0.01725	0.286
$A = 2.390$	$B = -0.294$		$P_0 = 51.44$ c.c.		$\mu = 1.60 D.$		

TABLE VIII
Tertioctylamine

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n_{12}^2	Δn^2 (-)	$\Delta n^2/w$ (-)
0.01243	2.2759	0.0119	0.955	1.49373	2.23122	0.00336	0.270
0.01972	2.2825	0.0185	0.938	1.49303	2.22913	0.00545	0.276
0.04153	2.3050	0.0410	0.988	1.49152	2.22463	0.00995	0.240
0.05181	2.3123	0.0483	0.931	1.49018	2.22064	0.01394	0.269
0.06963	2.3306	0.0666	0.956	1.48845	2.21547	0.01911	0.275
0.07893	2.3390	0.0750	0.950	1.48786	2.21373	0.02085	0.264
0.09919	2.3589	0.0949	0.957	1.48581	2.20763	0.02695	0.272
0.11660	2.3748	0.1108	0.950	1.48458	2.20397	0.03061	0.262
$A = 0.950$	$B = -0.206$		$P_0 = 29.79$ c.c.		$\mu = 1.22 D.$		

TABLE IX

Compound	Formula	Author μ_B	Literature μ_B	values μ_V
Ammonia	NH_3	—	1.40*	1.45D
Methylamine	CH_3NH_2	—	1.46	1.28
Ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	—	1.37	0.99
<i>n</i> -Propylamine	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	—	1.32	1.17*
<i>n</i> -Butylamine	$\text{CH}_3(\text{CH}_2)_3\text{NH}_2$	—	1.32	1.00*
sec-Butylamine	$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$	—	1.28	—
tert-Butylamine	$(\text{CH}_3)_3\text{CNH}_2$	—	1.29	—

<i>n</i> -Amylamine	$\text{CH}_3(\text{CH}_2)_4\text{NH}_2$	1.55	—	—
<i>n</i> -Hexylamine	$\text{CH}_3(\text{CH}_2)_5\text{NH}_2$	1.59	—	—
<i>n</i> -Heptylamine	$\text{CH}_3(\text{CH}_2)_6\text{NH}_2$	1.60	—	—
<i>n</i> -Octylamine	$\text{CH}_3(\text{CH}_2)_7\text{NH}_2$	1.42	—	—
<i>n</i> -Decylamine	$\text{CH}_3(\text{CH}_2)_9\text{NH}_2$	1.41	—	—
Isoamylamine	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{NH}_2$	1.53	—	—
Isohexylamine	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_4\text{NH}_2$	1.60	—	—
Tertioctylamine	$(\text{CH}_3)_3\text{CNH}_2(\text{CH}_2)_4$	1.22	—	—

*value of Le Fevre and Russell (1947)

**values of Barclay, Le Fevre and Smythe (1951)

 μ_B values in solution in benzene μ_V values in the vapour state.

gas values (i.e., a positive solvent effect). It is seen that for all the amines listed in Table IX for which the vapour values are available $\mu_B > \mu_V$. Cowley (1952) also observed a positive solvent effect for *n*-propyl and *n*-butyl amines in all the solvents he used. This may perhaps explain the values obtained in this investigation. But, when compared to the literature values on the lower members, the author's values appear to be slightly high for some of the molecules. The following points may be noted:

(1) As we go higher up in the homologous series, there is a tendency for a decrease in the moment. This is in conformity with the conclusions of Smith (1955b). As is already shown the resultant moment of the primary dipole is inclined at an angle of 100° with the C-N bond. Consequently there is rather a greater change of the induced moments opposing the primary moment than assisting it.

(2) The moments of the normal and iso- compounds are almost the same.

(3) The moment of the tertiary amines is a little less than that of the normal compound. A difference of 0.20 is obtained between *n*-octylamine and tert-octylamine. The corresponding difference is 0.11 for the butylamines (cf. Table IX).

(4) A small positive solvent effect in benzene appears reasonable. It is probable that a considerable change in the angle from 90° between the molecular dipole axis and the axis of maximum polarisability lowers the solvent effect so that the difference between vapour and solution values becomes much less.

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