Magnetic Study of the Amino Group

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The theoretical evaluation of the magnetic susceptibility may be done in two different ways (1) either by considering the atomic contribution of the constituent atoms of the molecule together with suitable constitutive correction or (2) by taking the compound as ionic and adding the contribution of ions. The former one has had wider applications than the latter. In the additive method the process suggested by Ingold[1] seems to be preferable due to the fact that it allows for the calculation, the contribution of atoms and multiple bonds as if there were no interactions. The difference between such calculated value and the experimental value is attributed as due to the interaction or conjugation involved in the system. The method suggested by Yang[2] on the other hand treats the shared electron in the covalent bond as ionic and the structures of molecules of covalent compounds are explained accordingly. But the method has got its own limitations as Yang himself pointed out that it requires, for example, different sets of paramagnetic susceptibilities for carbon ion. Still the method enables one to evaluate the contribution of different ions to the magnetic susceptibility.

In the present investigation, an attempt is made to evaluate the contribution due to NH_2^{1+}. Using this data, the χ_M of different compounds are calculated and compared with the experimental values and with theoretical values calculated by using the atomic and bond values suggested by Ingold. Any difference found from the experimental value has been explained as arising due to conjugation and interaction involved in the system. The contribution due to NH_2^{1+} can be found either from primary amines or from amino acids. In this investigation primary amines both aliphatic and aromatic have been studied.

Experimental

The substances used were mostly Merck G. R. or B. D. H.; A. R. The liquids were all distilled and collected exactly at the corresponding boiling

TABLE I*

S. No.	Substance	χ_S	χ_M Exptl.	χ_M Calcd.	$\Delta\chi_M$	χ_M-Others
1	Ethylenediamine	0.775 ±0.002	46.58	46.40	+0.18	
2	1, 2-Propylenediamine	0.780 ±0.002	57.82	58.20	−0.38	
3	Amylamine	0.834 ±0.001	72.73	73.30	−0.57	69.4[3]
4	Benzylamine	0.699 ±0.001	74.91	74.80	+0.11	72.01[4]
5	Ethanolamine	0.689 ±0.002	42.08	42.50	−0.42	
6	*o*-Chloroaniline	0.623 ±0.002	79.49	77.70	+1.79	
7	*m*-Chloroaniline	0.600 ±0.002	76.56	77.70	−1.14	
8	*p*-Chloroaniline	0.609 ±0.002	77.69	77.70	−0.01	
9	*o*-Ethylaniline	0.713 ±0.002	86.42	87.00	−0.58	
10	*p*-Ethylaniline	0.700 ±0.002	84.84	87.00	−2.16	
11	*o*-Anisidine	0.644 ±0.001	79.34	79.80	−0.46	80.56[5]
12	*m*-Anisidine	0.625 ±0.001	77.00	79.80	−2.80	
13	*p*-Anisidine	0.629 ±0.001	77.50	79.80	−2.30	
14	*o*-Nitroaniline	0.482 ±0.002	66.56	69.30	−2.74	66.47[6], 66.37[7], 68.42[8]
15	*m*-Nitroaniline	0.506 ±0.001	69.88	69.30	+0.58	70.19[6], 67.76[7], 68.96[8]
16	*p*-Nitroaniline	0.479 ±0.002	66.15	69.30	−3.15	60.42[6], 66.24[7], 66.82[8]

* All susceptibility values in this paper refer to diamagnetic susceptibility in 10^{-6} c. g. s. units.

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TABLE II. DIAMAGNETIC SUSCEPTIBILITY CONTRIBUTION OF THE $(NH_2)^{1+}$ ION

Substance	Experimental value	Neutralization of ions*	Contribution of NH_2^{1+}
Ethylenediamine	46.58	$M_2^{2-}+2(NH_2)^{1+}$	8.99
Benzylamine	74.91	$B^{1+}+M_1^{2-}+(NH_2)^{1+}$	8.25
1, 2-Propylenediamine	57.82	$M_3^{2-}+2(NH_2)^{1+}$	8.68
Ethanolamine	42.08	$NH_2^{1+}+M_1^{2-}+(CH_2OH)^{1+}$	8.19
n-Amylamine	72.73	$M_5^{1-}+(NH_2)^{1+}$	8.55

* The symbols used in column 3 are based on Yang's[2)] paper.

TABLE III

S. No.	Substance	Neutralization of ions	χ_M Calcd. (Yang)	χ_M Exptl.	$\Delta\chi_M$
1	*o*-Ethylaniline	$M_2^{1+}+B_{1,2}^{2-}+NH_2^{1+}$	87.02	86.42	−0.60
2	*p*-Ethylaniline	$M_2^{1+}+B_{1,4}^{2-}+NH_2^{1+}$	87.02	84.84	−2.18
3	*o*-Chloroaniline	$Cl^{1+}+B_{1,2}^{2-}+NH_2^{1+}$	77.49	79.49	+2.00
4	*m*-Chloroaniline	$Cl^{1+}+B_{1,3}^{2-}+NH_2^{1+}$	77.49	76.56	−0.93
5	*p*-Chloroaniline	$Cl^{1+}+B_{1,4}^{2-}+NH_2^{1+}$	77.49	77.69	+0.20
6	*o*-Anisidine	$B_{1,2}^{2+}+(O^{2-}M_1^{1+})^{1-}+\theta+NH_2^{1+}$	80.45	79.34	−1.11
7	*m*-Anisidine	$B_{1,3}^{2+}+(O^{2-}M_1^{1+})^{1-}+\theta+NH_2^{1+}$	80.45	77.00	−3.45
8	*p*-Anisidine	$B_{1,4}^{2+}+(O^{2-}M_1^{1+})^{1-}+\theta+NH_2^{1+}$	80.45	77.50	−2.95
9	*o*-Nitroaniline	$(NO_2)^{1+}+B_{1,2}^{2-}+NH_2^{1+}$	70.00	66.56	−3.44
10	*m*-Nitroaniline	$(NO_2)^{1+}+B_{1,3}^{2-}+NH_2^{1+}$	70.00	69.88	−0.12
11	*p*-Nitroaniline	$(NO_2)^{1+}+B_{1,4}^{2-}+NH_2^{1+}$	70.00	66.15	−3.85

point. The solids were all purified by standard methods and the purification was continued till specimens of constant susceptibility were obtained. Great care was taken to prevent absorption of atmospheric moisture.

Measurement of susceptibilities of the liquids were made with a Guoy[9)] balance. A correction has been applied for the residual air above the liquid surface. Since uniformity of packing is difficult to achieve in the case of solids the Curie[10)] retorsion method was preferred. A. R. benzene dried over sodium wire and distilled over phosphorus pentoxide was used as standard and its specific susceptibility was taken as -0.702×10^{-6} units.

Results

The results obtained for the amines are recorded in Table I, the observed values were the mean of six very closely agreeing values. The theoretical values (column 4) were calculated by taking atomic and bond values as given by Ingold[1)].

Evaluation of $(NH_2)^{1+}$ Contribution.—It is well known that in the aliphatic primary amines, the unshared electrons are in the tetrahedral orbital of non-interacting type. Hence the contribution of the $(NH_2)^{1+}$ has been derived from the experimental values of five such amines. In this evaluation the modified ionic values of Angus[11)] has been used wherever necessary. It has been further assumed that the removal of a proton does not affect the ionic susceptibilities. This evaluation from these amines gives fairly consistent values for the $(NH_2)^{1+}$ ion, and the values thus obtained are recorded in Table II. The average value of $(NH_2)^{1+}$ works out to be 8.50.

Discussion

The $(NH_2)^{1+}$ value thus obtained has been utilized to calculate χ_M by Yang's method for aromatic compounds. The values are given in Table III.

The last column gives the exaltations observed in the aromatic amines and these can be explained on the basis of molecular orbital theory. The exaltations that are observed is the result of two interactions arising due to the transfer of tetrahedral orbital of the 'N' atom to the p orbital which results in a negative exaltation and the intermingling of the p orbital of the substituting NH_2 group with the π orbital of the benzene ring which yields a positive exaltation. The NH_2^{1+} value was obtained from the aliphatic amines in which the 'N' atom is in the tetrahydral orbital and so the $\Delta\chi_M$ observed is due to the above mentioned interactions. The $\Delta\chi_M$ is negative in all the cases except in *o*-chloroaniline where it is +2.00. In ortho chloroaniline the intramolecular hydrogen bond keeps the molecule in plane and so the full effect of the p orbital with the aromatic π orbital results in a rather positive exaltation.

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9) S. R. Rao and A. S. Narayanasamy, *Proc. Ind. Acad. Sci.*, **9**, 35 (1939).

10) S. R. Rao, ibid., **A1**, 123 (1934).

11) W. R. Angus, *Proc. Roy. Soc.*, **A136**, 569 (1932).

Paramagnetic Contribution of N^{3+} Ion.—The close agreement among the calculated values by Yang's method and that of Ingold's additive method shows that the derived value of $(NH_2)^{1+}$ from aliphatic amines is consistent. Hence this value can be conveniently used for the derivation of the ionic susceptibility of the nitrogen ion N^{3+}.

$$(NH_2)^{1+} = -8.50$$

$$\chi_{N^{3+}} + 2\chi_{\theta} + 2\chi_{H^{1+}} = -8.50$$

Using the value of χ_{θ} as -4.88

$$\therefore\ \chi_{N^{3+}} = +1.26$$

Thus we are led to the conclusion that the ion N^{3+} posseses a paramagnetic susceptibility value. But Angus[11] gives a value of -2.09. The paramagnetic value that is obtained by Yang's method for the ion N^{3+} has been utilized and calculated for triethylamine.

$$\chi_{(C_2H_5)_3N} = \chi_{N^{3+}} + 3\chi_{M_2{}^{1-}} = -84.54$$

The additive method based on Ingold's value gives χ_M as 85.1 which is in fair agreement with that of the value obtained by Yang's method.

Summary

The diamagnetic susceptibilities of several aliphatic and aromatic amines have been determined. The susceptibility contribution, of $NH_2{}^{1+}$ is evaluated from the noninteracting aliphatic amines, and this value is used for calculation of χ_M of aromatic amines. The exaltations are attributed to the interactions in the system. An anomalous value for N^{3+} ion is obtained.

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