Magnetic Study of Nitro Group

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Introduction of a substituent group for hydrogen in a benzene ring generally resulted a small but detectable change in various physical constants. But the nature of the effect depended much on the position of the group in the ring, and also on the substituting group itself. When a large group like that of the nitro group is substituted in the benzene ring, such changes are found to be large and detectable. Certain anomalous effects were also noticed by different workers, in the case of nitro group. Abe[1] found that *m*-dinitrobenzene showed the maximum absorption band at shorter wavelengths than nitrobenzene. Such a result was also confirmed by Semba.[2] He also measured the equilibrium constants of isomeric nitroanilines and found that the meta compound had a very high value compared with other two isomers. These differences were attributed to the meta-directing property of the nitro group. The resonance structures of the nitro group was also found to contribute largely to the observed changes in the ultraviolet spectrum. Jatkar and Phansalker[3] from their measurements of dipole moments of the nitro-substituted compounds confirmed that the meta directing inductive effect of the nitro group had a considerable influence on the dipole moment.

Bhatnagar and his collaborators[4] detected a variation in the diamagnetic susceptibility depending on the position of the substituting group in the benzene ring, ortho showing a maximum value. Later Cabrera and Fahlenbrach[5] found that in nitrotoluenes the meta compound had a higher value of χ_M than the other two isomers. French,[6] after studying a large number of compounds, noticed an anomalous effect in the case of nitro-substituted compounds. This anomaly was explained by Baddar and Mikhail[7] and later by Mikhail[8], as arising from the contribution of the quinonoid structures of the nitro group to the normal structure. The contribution of the nitro group to the diamagnetic susceptibility was found to vary from 1.45 to 11.74 by Shah et al.[9] But Sriraman and Sabesan[10] found that the behavior of the nitro group, when substituted in the benzene ring, fell generally in line with the observations made by Mikhail,[8] and no serious irregularities were noticed by them. The large changes reported by Shah et al.[9] could not be explained

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TABLE I

No.	Substance	Mol. wt.	χ_s	χ_M, Exptl.	χ_M, Calcd.	$\Delta\chi_M$	χ_M	Other values	
1	*o*-Dinitrobenzene	168.11	0.398 ± 0.002	66.91	66.70	+0.21	65.98_6	74.3_{13}	
2	*m*-Dinitrobenzene	168.11	0.424 ± 0.002	71.29	66.70	+4.59	70.53_6	72.8_{13}	
3	*p*-Dinitrobenzene	168.11	0.399 ± 0.002	67.08	66.70	+0.38	68.30_6	70.6_{13}	
4	*o*-Chloronitrobenzene	157.56	0.479 ± 0.001	75.50	75.10	+0.40	80.65_9		
5	*m*-Chloronitrobenzene	157.56	0.490 ± 0.001	77.23	75.10	+2.13	76.07_9	74.70_{14}	
6	*p*-Chloronitrobenzene	157.56	0.474 ± 0.001	74.71	75.10	−0.39	79.54_9		
7	*o*-Nitroanisole	153.13	0.518 ± 0.001	79.30	77.20	+2.10	75.28_9		
8	*p*-Nitroanisole	153.13	0.511 ± 0.002	78.23	77.20	+1.03	79.25_9		
9	*o*-Nitrotoluene	137.13	0.523 ± 0.002	71.69	70.60	+1.09	71.85_5	72.19_9	72.28_7
10	*m*-Nitrotoluene	137.13	0.541 ± 0.002	74.16	70.60	+3.56	72.42_5	72.61_9	72.71_7
11	*p*-Nitrotoluene	137.13	0.527 ± 0.002	72.24	70.60	+1.64	70.89_5	69.87_9	72.06_7
12	*o*-Nitroaniline	138.12	0.482 ± 0.002	66.56	67.30	−0.74	68.42_7	66.475_8	66.37_8
13	*m*-Nitroaniline	138.12	0.506 ± 0.001	69.88	67.30	+2.58	68.96_7	70.19_8	67.76_9
14	*p*-Nitroaniline	138.12	0.479 ± 0.002	66.15	67.30	−1.15	66.82_7	60.425_8	66.24_9
15	*o*-Nitrophenol	139.11	0.491 ± 0.002	68.29	65.40	+2.89	70.20_9		
16	*m*-Nitrophenol	139.11	0.498 ± 0.002	69.26	65.40	+3.86	65.60_9		
17	*p*-Nitrophenol	139.11	0.486 ± 0.002	67.59	65.40	+2.19	63.39_9	67.00_{14}	

TABLE II

No.	Substance	Formula	Neutralization of ions*	χ_M Exptl.	$(\chi_M - NO_2)$ Calcd.	Contribution $(NO_2)^{1+}$
1	*o*-Dinitrobenzene	$C_6H_4 \cdot NO_2 \cdot NO_2$	$B^{2-}1,2+2(NO_2)^{1+}$	66.91	54.80	6.06
2	*m*-Dinitrobenzene	$C_6H_4 \cdot NO_2 \cdot NO_2$	$B^{2-}1,3+2(NO_2)^{1+}$	71.29	54.80	8.25
3	*p*-Dinitrobenzene	$C_6H_4 \cdot NO_2 \cdot NO_2$	$B^{2-}1,4+2(NO_2)^{1+}$	67.08	54.80	6.14
4	*o*-Chloronitrobenzene	$C_6H_4 \cdot Cl \cdot NO_2$	$B^{2-}1,2+Cl^{1+}+(NO_2)^{1+}$	75.50	68.99	6.51
5	*m*-Chloronitrobenzene	$C_6H_4 \cdot Cl \cdot NO_2$	$B^{2-}1,3+Cl^{1+}+(NO_2)^{1+}$	77.23	68.99	8.24
6	*p*-Chloronitrobenzene	$C_6H_4 \cdot Cl \cdot NO_2$	$B^{2-}1,4+Cl^{1+}+(NO_2)^{1+}$	74.71	68.99	5.72
7	*o*-Nitroanisole	$C_6H_4 \cdot OCH_3 \cdot NO_2$	$B^{2+}1,2+(O^{2-}M_1^{1+})^{1-}+(\theta NO_2)^{1-}$	79.30	71.95	7.35
8	*p*-Nitroanisole	$C_6H_4 \cdot OCH_3 \cdot NO_2$	$B^{2+}1,4+(O^{2-}M_1^{1+})^{1-}+(\theta NO_2)^{1-}$	78.23	71.95	6.28
9	*o*-Nitrotoluene	$C_6H_4 \cdot CH_3 \cdot NO_2$	$B^{2-}1,2+M^{1+}+(NO_2)^{1+}$	71.69	66.66	5.03
10	*m*-Nitrotoluene	$C_6H_4 \cdot CH_3 \cdot NO_2$	$B^{2-}1,3+M^{1+}+(NO_2)^{1+}$	74.16	66.66	7.50
11	*p*-Nitrotoluene	$C_6H_4 \cdot CH_3 \cdot NO_2$	$B^{2-}1,4+M^{1+}+(NO_2)^{1+}$	72.24	66.66	5.58
12	*o*-Nitrophenol	$C_6H_4 \cdot OH \cdot NO_2$	$B^{2+}1,2+(\theta NO_2)^{1-}+OH^{1-}$	68.29	61.17	7.12
13	*m*-Nitrophenol	$C_6H_4 \cdot OH \cdot NO_2$	$B^{2+}1,3+(\theta NO_2)^{1-}+OH^{1-}$	69.26	61.17	8.09
14	*p*-Nitrophenol	$C_6H_4 \cdot OH \cdot NO_2$	$B^{2+}1,4+(\theta NO_2)^{1-}+OH^{1-}$	67.59	61.17	6.42

* The symbols used in column 4 are based on Yang's[16] paper.

satisfactorily, and therefore it was believed that a careful examination of the diamagnetic contribution of the nitro group, taking some more compounds also, might be of interest.

Experimental

The investigations were carried out with a Curie balance.[11] A. R. benzene dried over sodium and distilled over phosphorus pentoxide was used as standard. Its specific susceptibility was taken as -0.702×10^{-6} units. Liquids and solids were purified by standard methods and the purification was continued till specimens of constant susceptibility were obtained. The purified substance was filled in thin-walled glass bulbs, the remaining portion of the bulb being completely evacuated. The solids are powdered and then filled up in the bulb to eliminate orientation effects.

Results

Magnetic susceptibilities of seventeen substances are given in Table I. The observed values are the mean of eight very closely agreeing values, the maximum deviation being shown in the same table. The last column refers to the χ_M values recorded by other workers and is given for the sake of comparison. The theoretical values were calculated by taking atomic and bond values as given by Ingold.[12]

Discussion

In all the nitro compounds studied it is seen that in all cases the meta compound has a higher χ_M value than the other two isomers. Such a result is normally expected as already explained by Sriraman and Sabesan[10]. Also the difference between the experimental values of χ_M and theoretically calculated values are less than two units in most cases and for only a few compounds $\Delta\chi_M$ exceeds three units. This definitely shows that there is no large irregularity in the behavior of the nitrosubstituted compounds and these small differences are explicable by taking into account the inductive and resonance effects[10].

The Contribution of the Group $(NO_2)^{1+}$.— Sriraman and Shanmugasundaram[15] calculated the contribution of the $(NH_2)^{1+}$ value to the diamagnetic susceptibility by treating the shared electrons of the covalent bond as ionic as suggested by Yang[16]. A similar attempt is made to calculate the contribution of $(NO_2)^{1+}$ by taking Angus' modified ionic value[17].

It has been found that the contribution of $(NO_2)^{1+}$ group to the diamagnetic susceptibility, when substituted in the meta position is about eight units and the average contribution is 6.7 units. The atomic contribution of nitro group in organic nitrates was found to be 5.6 by Voiget[18] but in organic nitro compounds he obtained a value of 8.7 units. But the present value of 6.7 units (on the average) for $(NO_2)^{1+}$ is in accordance with the value given by Yang[16] (6.57 units).

The χ_M value of CH_2 when it combined with O^{2-} was taken by Yang as 10.78 units. It is worthy to note that in our present investigation, (χ_M nitroanisole $-\chi_M$ nitrophenol) in ortho and para isomeric compounds are 11.01 and 10.64 respectively, making an average of 10.83, a value very similar to the one obtained by Yang. This arguement cannot be substantiated at this stage until more work is done in this direction.

Summary

The magnetic susceptibilities of several disubstituted aromatic nitro compounds were determined by Curie retorsion method. The contribution of the $(NO_2)^{1+}$ to the diamagnetic susceptibility was evaluated by the method suggested by Yang, taking Angus' modified ionic values.

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