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On the Physicomagnetic Properties of Some Nitro Compounds

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The mean molar susceptibilities of nine aromatic nitro compounds namely, *o*-, *m*-, *p*-dinitrobenzene; *o*-, *m*-, *p*-nitrobenzoic acid and *o*-, *m*-, *p*-nitrophenol have been measured. The semiexperimental anisotropies of these molecules have been calculated. The magnetic data are correlated with the positional isomerism of the nitro groups and the crystal structures of these molecules as well as their hydrogen bonding.

Introduction of a large group like that of the nitro group (NO_2) for hydrogen atom in a benzene ring generally resulted in a detectable change in various physical constants of the molecule. But the nature of the effect depends much on the position of the group in the ring. The mean molar susceptibilities of the nitro group and nitro compounds have been extensively considered theoretically or experimentally. Cabrena and Fahlenbrach[1] found that, in nitrotoluene, the *m*-compound had a higher value of the observed molar susceptibility (χ_M^{obsd}) than the other two isomers. French[2] after studying a large number of compounds, noticed an anomalous effect in the case of nitro-substituted compounds. This anomaly was explained by Badder and Mikhail[3] and later by Mikail,[4] as arising from the contribution of the quinonoid structures of the nitro group to the normal structure. From their measurements of the χ_M^{obsd} of seventeen aromatic nitro compounds, Sriraman *et al.*[5] found that the contribution of the nitro group to the mean susceptibilities depends on its position on the benzene ring.

We felt that, it is of interest to study the contribution of the nitro group to the magnetic anisotropies of some benzenoid molecules semiexperimentally. The large anisotropies of the diamagnetic susceptibilities of benzenoid molecules are usually interpreted in terms of ring currents[6—10] despite some criticism.[11,12] A recent paper on the use of the ring current concept has been given by Gomes.[13]

If K_1, K_2, and K_3 are the principal molecular susceptibilities, (K_1, K_2) are the in-plane susceptibility and K_3 is the out-of-plane susceptibility, then the magnetic anisotropy of a molecule is defined as:

$$\Delta K = K_3 - \frac{1}{2}(K_1+K_2) \qquad (1)$$

In general, the molecular susceptibilities (and hence the magnetic anisotropy) can be estimated by measuring the principal crystal susceptibilities (χ_1, χ_2, χ_3) combined with the information about the orientation of the molecules in it. The mathematical relations concerning the transition from crystalline to molecular susceptibilities were previously given by Lonsdale and Krishnan.[14]

In the present work, the magnetic anisotropies of these molecules have been calculated semiexperimentally. The details of this method have been discussed before by one of the present authors.[15] The equation used is

$$\Delta K_{semi} = 3[\chi_M^{obsd} - \frac{1}{2}(K_1+K_2)]. \qquad (2)$$

Experimental

The molecules studied in this paper can be classified into three groups:

1) Dinitro Benzenes: a) *o*-Dinitrobenzene.[16] b) *m*-Dinitrobenzene.[17] c) *p*-Dinitrobenzene.[18]

2) Nitrobenzoic Acids: a) *o*-Nitrobenzoic acid.[19] b) *m*-Nitrobenzoic acid.[20] c) *p*-Nitrobenzoic acid.[21]

3) Nitrophenols: a) *o*-Nitrophenol.[22] b) *m*-Nitrophenol. c) *p*-Nitrophenol.[23]

The crystal structure of these compounds are known except for *m*-nitrophenol. The purity of each compound was tested by measuring its melting point. Purification by recrystallization from solvents was carried out when the melting point of the compound is slightly different from that given in the literatures. The melting point (mp) of each compound has been given in Table 1.

The Gouy method was employed for the measurements of the susceptibility of each compound. Details of this method has been given elsewhere.[15]

Results and Discussion

In Table 1, the specific susceptibility χ_S, the observed

TABLE 1. OBSERVED AND CALCULATED SUSCEPTIBILITIES ($\times 10^{-6}$ emu mol^{-1})

Compound	Mp θ_m/°C	Mol wt	χ_S	χ_M^{obsd}	χ_M^{calcd}	$\Delta\chi_M$	Other values
o-Dinitrobenzene	118	168	−0.400±0.002	−67.20	−69.48	−2.28	−65.98[a],−66.91[b]
m-Dinitrobenzene	89—90	168	−0.424±0.001	−71.23	−69.48	+1.75	−70.53[a],−71.29[b]
p-Dinitrobenzene	173.5	168	−0.405±0.001	−68.04	−69.48	−1.44	−68.30[a],−67.08[b]
o-Nitrobenzoic acid	147	167	−0.462±0.001	−77.15	−77.54	−0.39	−76.11[a],−77.03[c]
m-Nitrobenzoic acid	140	167	−0.485±0.002	−80.99	−77.54	+7.45	−80.22[a],−77.19[c]
p-Nitrobenzoic acid	238	167	−0.468±0.002	−78.16	−77.54	+0.62	−78.81[a],−77.86[c]
o-Nitrophenol	45	139	−0.478±0.001	−66.44	67.04	−0.6	−67.39[b]
m-Nitrophenol	96	139	−0.494±0.002	−68.67	67.04	+1.63	−69.40[b]
p-Nitrophenol	113	139	−0.476+0.002	−66.16	67.04	−0.88	−67.00[b]

a): Ref. 2, b): Ref. 5, c): *Sci. Rep. Tohoku Imp. Univ.*, **24**, 701 (1936).

Table 2. Semiexperimental magnetic anisotropic ($\times 10^{-6}$ emu mol^{-1})

Compound	$\sum\chi_A$	$\frac{1}{2}(K_1+K_2)$ $=\chi_A+n\propto$	K_3	$\Delta K'^{a)}$ $=K_3-\sum\chi_A$	ΔK_{semi}
o-Dinitrobenzene	−70.68	−47.88	−105.84	−35.16	−57.96
m-Dinitrobenzene	−70.68	−47.88	−117.93	−47.25	−70.05
p-Dinitrobenzene	−70.68	−47.88	−108.36	−37.68	−60.48
o-Nitrobenzoic acid	−80.14	−53.54	−124.37	−44.23	−70.83
m-Nitrobenzoic acid	−80.14	−53.54	−135.89	−55.75	−82.35
p-Nitrobenzoic acid	−80.14	−53.54	−127.40	−47.26	−73.86
o-Nitrophenol	−68.14	−45.34	−108.64	−40.50	−63.30
m-Nitrophenol	−68.14	−45.34	−115.33	−47.19	−69.99
p-Nitrophenol	−68.14	−45.34	−107.86	−39.72	−62.46

a) The calculated values of $\Delta K'$ and/or ΔK_{semi} for the benzene ring and/or the acid molecule were given in Ref. 15.

molar susceptibility χ_M^{obsd} and the calculated molar susceptibility χ_M^{calcd} of each compound are presented.

The method used for the calculation of χ_M (in 10^{-6} emu mol^{-1}) is as follows:

a) The mean molar susceptibility of the benzene ring is −55.20.[10]

b) The drop in diamagnetism of the benzene ring due to the replacement of one hydrogen atom by another atom or group is 2.00.

c) The mean molar susceptibility of the $(NO_2)^{1+}$ group is −6.7,[5] using Yung method,[24] we get for the neutral NO_2 group the value $-(6.7+2.44)=-9.14$.

d) The mean molar susceptibility of the COOH group is −17.20[25] and of the OH group is 6.7.[25]

Thus the calculated molar susceptibility of any molecule of the compounds of the first series is $(-55.20+2.00\times2-9.14\times2)=-69.48$.

The most important fact emerging from the data shown in Table 1 is that, the *m*-compound has a markedly higher diamagnetic susceptibility than the other two isomers. Such a result is normally expected. According to French,[2] Sriraman *et al.*,[5,26] and Baliah *et al.*,[27] the nitro group is strong meta-directing. When such group is substituted in the benzene ring, it tends to withdraw electrons from the ring and the displacement of electrons is mainly from the *o*- and *p*-positions. As a result, the *m*-position is the point of relatively high electron density which will mean a higher χ_M^{obsd} value for the *m*-isomer. It can also be seen from Table 1 that, the order of χ_M^{obsd} for the members of the first and second series is:

meta>para>ortho,

as suggested by Baliah *et al.*[27] in a similar work. For the compounds of the third series, the OH group is *o*, *p*-directing and the NO_2 group is strong *m*-directing, so the order of χ_M^{obsd} is

meta>ortho>para.

Recently,[28] a different theoretical approach, where the susceptibility is represented as a sum of bond contributions and bond-bond interaction is capable of explaining difference between isomers.

The values of $\frac{1}{2}(K_1+K_2)$, K_3 or $K^{\perp}$, and ΔK_{semi} for each compound are listed in Table 2. The values of the atomic susceptibilities used in the calculations of $\sum\chi_{atomic}$ are:

$$\chi_C = -7.4,^{29)}\ \chi_H = -2.0,^{29)}\ \chi_O = -4.6.^{30)}$$

For the NO_2 group, its magnetic susceptibility depends on its position in the benzene ring,[5] its value is taken as −9.14.

Perhaps the most striking fact emerging from the magnetic data of the compounds of the first series given in Table 2 is that the semiexperimental magnetic anisotropy of the *m*-dinitrobenzene is numerically too high. Fortunately, the observed magnetic data of this compound have been determined by Lasheen.[31] Accordingly,

$$K_L \equiv (K_1) = -50 \pm 6.9,\ K_M \equiv (K_2) = -41.7 \pm 2.1,$$

$$K_N \equiv K_3 = -119.8 \pm 6.7 \text{ and } \Delta K_{obsd} = -74 \pm 7.6.$$

Unfortunately Lasheen did not give any explanation for his results because he was interested only in the molecular susceptibilities. The semiexperimental magnetic anisotropy of *m*-dinitrobenzene agrees closely with Lasheen value. Furthermore, our results for $K^{//}$ and $K^{\perp}$ are also in agreement with Lasheen values. This can be considered as a check on the accuracy of the semiexperimental method.

Since the *m*-dinitrobenzene crystals are orthrhombic, therefore the crystallographic axes agree with the axes of the triaxial ellipsoid representing the crystal susceptibilities (χ_a, χ_b, and χ_c). Assuming $K_1 \simeq K_2$, the values of χ_a, χ_b, and χ_c have been calculated by the present authors from the set of equations given in Ref. 15. Our values for χ_a, χ_b and χ_c are

$$\chi_a = -48.34,\ \chi_b = -59.40,\ \chi_c = -105.84.$$

In a good agreement with Lasheen experimental values namely,

$$\chi_a = -45.1 \pm 2.3,\ \chi_b = -58.9 \pm 2.4,$$

$$\chi_c = -107.05 \pm 4.6.$$

In the opinion of the present authors, there are two possibilities for the interpretation of the high value of ΔK for this compound:

a) The NO_2 group is not magnetically isotropic and may have a certain value of anisotropy like for example the carbonate or nitrate groups.[32]

b) The second possibility which seems to us more likely to exist is the dipole moment of the molecule. Since we have two NO_2 groups, therefore the dipole moment of the molecule will depend largely on the positions of the two NO_2 groups relative to each other. From their measurements of the dipole moment of the nitro-substituted compounds, Jalkar and Phansalker[33] confirmed that the m-directing inductive effect of the nitro group had a considerable influence on the dipole moment.

At this point, it is necessary to calculate the delocalization anisotropy or the π-electron susceptibility. The results of calculations are given in Table 2. The empirical equation used for these calculations is that given by Davies,[34] namely

$$\Delta K' = K^{\perp} - \sum\chi_{\text{atomic}}.$$

From Table 2, it is clear that the delocalization anisotropy of the m-isomer is numerically much higher than that of the benzene ring and of the other two isomers. In other words the effect of the NO_2 groups in the m-position to the magnetic properties of the molecule is much more pronounced than that of the other two isomers.

For the members of the second and third series it is of interest to correlate the magnetic properties of these molecules with their structures and their hydrogen bonding systems. Refinements of the crystal structures of the nitrobenzoic acid molecules have been carried out by the Indian group, Pant *et al.*[19–21] The general feature of the crystal structures of these molecules is that, the acid groups are dimerized across intermolecular hydrogen bonds. The O–H···O are 2.645 and 2.653 Å for o- and p-nitrobenzoic acids respectively. For the m-nitrobenzoic acid, each dimeric unit consisting of crystallographically independent molecules A and B. The O–H···O hydrogen bonds linking molecules A and B are 2.630 and 2.666 Å.[29]

The contribution of the hydrogen bonding to both the magnetic susceptibilities and anisotropies of some aromatic compounds containing a benzene ring has been discussed by the present authors,[15,35] We have showed that the effect of the hydrogen bonding is to increase the values of $\Delta K'$ and/or ΔK of the acid molecule by about 5×10^{-6} emu mol^{-1}. from the calculated one. Thus for the o- and/or p-nitrobenzoic acid the numerical increase in $\Delta K'$ and/or ΔK of the molecule can be ascribed to the additional magnetic anisotropy of the electron delocalization resulting from the hydrogen bonding as suggested by Mason.[29]

The case of m-nitrobenzoic acid is very intersting. For this compound, the values of $\Delta K'$ and/or ΔK are numerically much greater than that of the other two isomers. Since the hydrogen bonding scheme of the three nitrobenzoic acid molecules are similar,[19–21] therefore one cannot attribute this large anisotropy to the effect of the hydrogen bonding alone. In other words, the contribution of the NO_2 group in this case (*i.e.* in the m-position) to the anisotropy of the molecule is very clear.

For the compounds of the third series, the hydrogen bonds are due to the OH and/or NO_2 group. This type of hydrogen bonding is much weaker than that of the COOH group. Thus the slight increase in the anisotropies of the o- and/or p-nitrophenol can be explained as resulting from the contribution of the weak hydrogen bonding of these molecule. On the other hand, the anisotropy of the m-nitrophenol is numerically much greater than that of the o- and/or p-isomers and cannot be ascribed to the effect of hydrogen bonding alone.

In conclusion, the observed molar susceptibilities and the magnetic anisotropies of the m-nitro compounds are numerically much greater than that of the o- and/or p-isomers. These peculiar magnetic properties of the m-nitro compounds may be attributable to the large dipole moments of the m-isomers or probably to the anisotropy of the nitro group in the m-position. Certain anomalous effects which agree and support this conclusion were found by other workers. Abe[36] found that m-dinitrobenzene showed the maximum absorption band at shorter wavelengths than nitrobenzene, such a result was also confirmed by Semba.[37] He also measured the equilibrium constants of isomeric nitroanilines and nitrophenol, and found that the meta compound had a very high value compared with other two isomers.

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