Semiexperimental Magnetic Study of Some Methyl Derivatives of Benzoic Acid

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The mean molar susceptibilities of some methyl derivatives of benzoic acid have been measured. From these measurements and the calculated value of the in-plane susceptibilities (K_1, K_2) of each molecule, the semiexperimental magnetic anisotropy of the acid molecule has been determined. The obtained magnetic data are explained on the basis of the hydrogen bonding systems of these molecules.

The peculiar magnetic properties of aromatic compounds (besides exaltation, there are large magnetic anisotropies and anomalous nmr chemical shifts) are widely held to be results of the relatively large magnetic moment induced in the fully delocalized π-electrons characteristic of these molecules.[1-3] This has come to be called the "ring current." The contribution of the ring current to the magnetic susceptibility is amenable to theoretical calculation. The literature in this field is extensive.[4-9]

Although the contribution of the ring current to the magnetic susceptibility is comparatively large and is the main cause of the anisotropy of the diamagnetic susceptibility of a molecule,[6] yet other contribution of σ-electrons and localized π-electrons are also important.[10] Hoarau[11] suggested that the ring current probably accounts for not more than half of the observed anisotropy of benzene. He discussed the anisotropy of benzene and other aromatic hydrocarbons according to the scheme:

$$\Delta K_{\text{obsd}} = \Delta K_{\text{London}} + \Delta K_{\sigma} + n\Sigma\Delta K_{\pi}. \quad (1)$$

The first term is the anisotropy according to London theory, *i.e.* the component due to the ring currents in the delocalized π-electrons; the second term represents the anisotropy due to σ-electrons, and the third term is the sum of anisotropies due to localized π-electrons. The effect of the last term is to increase the anisotropy, not through the usual enhancement of the out-of-plane susceptibility (K_3), but by a decrease in the in-plane susceptibilities K_1 and K_2. Davies[10] calculated the π-electron susceptibility ΔK^{π} of benzene and other system and gave the empirical equation:[12]

$$\Delta K^{\pi} = K_3 - \Sigma\chi_{\text{atomic}}, \quad (2)$$

where K_3 is the experimental out-of-plane susceptibility. A more recent calculation of ΔK^{π} was given by Edwards and McWeeny.[6] A complete discussion of the use of ring current concept in the magnetic susceptibility, magnetic anisotropy and nmr chemical shift was given recently by Gomes.[13]

In general, the principal susceptibilities (K_1, K_2, and K_3) and therefore the anisotropy of the diamagnetic susceptibility for a molecule can be found from the measured values of the crystal susceptibilities (χ_1, χ_2, and χ_3) along the principal axes of the crystals, combined with the orientation of the molecule in it. The set of equations that commonly used is:

$$\left.\begin{aligned}\chi_1 &= K_1\cos^2\alpha_1 + K_2\cos^2\alpha_2 + K_3\cos^2\alpha_3,\\ \chi_2 &= K_1\cos^2\beta_1 + K_2\cos^2\beta_2 + K_3\cos^2\beta_3,\\ \chi_3 &= K_1\cos^2\gamma_1 + K_2\cos^2\gamma_2 + K_3\cos^2\gamma_3,\end{aligned}\right\} \quad (3)$$

where ($\cos\alpha_1$, $\cos\beta_1$, and $\cos\gamma_1$) are the direction consines of K_1 relative to the axes of the triaxial ellipsoide. These direction consines are determined from the atomic coordinates as given by X-ray structure analysis, but after performing the transformation needed for systems other than the orthogonal one. Several investigators have been made in this way.[14-21] According to Akamatu,[3] such a method is the orthodox one. Recently both the magnetic susceptibility and the anisotropy are calculated semiemperically or theoretically.[6-8,22-24]

In this paper, the method suggested by Hoarau[11] is used. Accordingly, the value of $(1/2)(K_1+K_2)_{\text{calcd}}$ is given by:

$$(1/2)(K_1+K_2)_{\text{calcd}} = \Sigma\chi_{\text{atomic}} + n\alpha, \quad (4)$$

where n is the number of trigonally hybridized carbon atoms and α is a constitutive correction ($\simeq +3.8\times 10^{-6}$ emu mol^{-1}) expressing quantitatively the effect of ΔK_{π} of Eq. 2 on the in-plane susceptibilities.

Since the magnetic anisotropy of a molecule is given by

$$\Delta K = K_3 - (1/2)(K_1+K_2),$$

and

$$\chi_M^{\text{obsd}} = (1/3)(K_1+K_2+K_3),$$

therefore

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

Experimental

The compounds studied in this paper are:
a) *o*-Methylbenzoic acid (*o*-Toluic acid).[25]
b) *m*-Methylbenzoic acid (*m*-Toluic acid).[26]
c) *p*-Methylbenzoic acid (*p*-Toluic acid).[27]

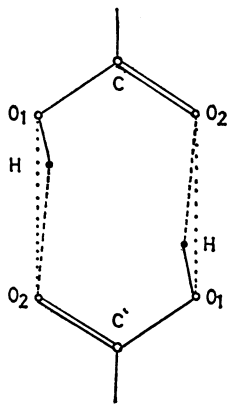

Fig. 1. The 8-membered ring.

d) 2,6-Dimethylbenzoic acid.[28]
e) 3,5-Dimethylbenzoic acid.[29]
f) 2,3,4-Trimethylbenzoic acid.[26]
g) 2,4,6-Trimethylbenzoic acid.[30]
h) 3,4,5-Trimethylbenzoic acid.[31]

The unit cell parameters of these compounds were previously obtained by different authors.[25-31] The purity of these compounds was tested by measuring their melting points. Purification by vacuum distillation and/or recrystallization from suitable solvents were carried out when the melting point of the compound is slightly different from those given in the literatures.

The Gouy method was employed for the measurements of the mean magnetic susceptibility of each compound. The apparatus consists essentially of an electromagnet and a sensitive Mettler balance. The magnetizing current is taken from a stabilized unit supplied with the electromagnet. The degree of stability of current amounts to 10^{-4}. The electromagnet is kept in a glass cabinet on top of which a sensitive Mettler balance is placed.

The purified material was finely powdered and was uniformally packed in the specimen tube. The later was made of Monax glass fitted with a glass stopper. The specimen in its container was suspended from one arm of the Mettler balance whose accuracy is 10^{-5} g. Suspension was done such that the tube is symmetrical with the pole pieces; its bottom being in the strong part of the field and the top well outside the field gap. The effect of the container and the correction of porosity of the packed powder were taken into account. Among a series of measurements, the calibration was checked with naphthalene and with benzoic acid.

In the Gouy method random orientation might be assumed since good powdering and packing were followed. The results obtained from adopting such a procedure gave consistent diamagnetic susceptibilities values with accuracy better than 1%.

Results and Discussion

The specific susceptibility χ_s, the observed molar susceptibility χ_M^{obsd} and the calculated molar susceptibility χ_M^{calcd} according to Pascal-Pacult method are given in Table 1. The atomic susceptibilities and the constitutive corrections (in 10^{-6} emu mol^{-1}) used in these calculations are:

$$\chi_C = -7.4,\ \chi_H = -2.0,\ \chi_{C\begin{smallmatrix}/O\\ \backslash O\end{smallmatrix}} = -15.15,$$

$$\chi_O = -5.30,\ \lambda_{benzene} = -1.40,\ \lambda_{CH_3} = -0.85$$

These values were given by Hoarau. For the CH_3 group, its magnetic susceptibility is taken as -13.24×10^{-6} emu mol^{-1}.[32]

It can be seen from Table 1 that the observed values of the molar susceptibilities of the *o*-, *m*-, and *p*-methylbenzoic acid are not equal. The slight difference (about one unit) in the χ_M^{obsd} of the *o*- and *m*-compound can be explained in terms of positional isomerism. According to Sriraman,[33] the CH_3 group is *o-p* directing and when substituted in the benzene ring gives higher value for ortho than for meta or isomers. The order of susceptibility should therefore be *o*->*p*->*m*-. French[34] pointed out that such an order should normally be expected. Since the CH_3 group is not strong *o-p* directing and no evidence exists for resonance in these compounds,[24,27] therefore the difference in χ_M^{obsd} is expected to be small. The results shown in Table 1 support these rules.

In Table 2, the values of $(1/2)(K_1+K_2)$, the out-of-plane susceptibility (K_3) and the semiexperimental magnetic anisotropy (ΔK_{semi}) of each compound are listed. For the benzoic acid, $\chi_M^{obsd} = -71.00\times 10^{-6}$ emu mol^{-1}, $(1/2)(K_1+K_2)_{calcd} = -47.80\times 10^{-6}$ emu mol^{-1}

Table 1. Observed and calculated magnetic susceptibilities[a]

Compound	Mol wt	χ_s	χ_M^{obsd}	χ_M^{calcd}	$\Delta\chi_M$
o-Methylbenzoic acid	136	−0.6117±0.001	−83.20	−85.04	−1.84
m-Methylbenzoic acid	136	−0.6036±0.001	−82.10	−85.04	−2.94
p-Methylbenzoic acid	136	−0.6073±0.002	−82.60	−85.04	−2.44
2,6-Dimethylbenzoic acid	150	−0.6300±0.002	−94.50	−97.13	−2.63
3,5-Dimethylbenzoic acid	150	−0.6240±0.001	−93.60	−97.13	−3.53
2,3,4-Trimethylbenzoic acid	164	−0.6420±0.001	−105.30	−109.22	−3.90
2,4,6-Trimethylbenzoic acid	164	−0.6451±0.002	−105.80	−109.22	−3.42
3,4,5-Trimethylbenzoic acid	164	−0.6402±0.001	−105.00	109.22	−4.22

a) Throughout this paper all values of χ's, K's, $\Delta\chi$'s and ΔK's are to be multiplied by 10^{-6} emu mol^{-1}.

Table 2. Semiexperimental magnetic anisotropies

Compound	$\Sigma\chi_{atomic}$	$(1/2)(K_1+K_2)_{calcd}$	K_3	ΔK_{semi}
o-Methylbenzoic acid	−85.8	−59.20	−131.20	−72.00
m-Methylbenzoic acid	−85.8	−59.20	−127.90	−68.70
p-Methylbenzoic acid	−85.8	−59.20	−129.40	−70.20
2,6-Dimethylbenzoic acid	−97.20	−70.60	−142.30	−71.70
3,5-Dimethylbenzoic acid	−97.20	−70.60	−139.60	−69.00
2,3,4-Trimethylbenzoic acid	−108.60	−82.00	−151.90	−69.90
2,4,6-Trimethylbenzoic acid	−108.60	−82.00	−153.40	−71.40
3,4,5-Trimethylbenzoic acid	−108.60	−82.00	−151.00	−69.00

TABLE 3. CONTRIBUTION OF THE HYDROGEN BONDING

Compound	ΔK_{mol}	$\Delta K_{benzene}$	Δ	ΔK_{semi}	ΔK_{calcd}	Δ
o-Methylbenzoic acid	−45.40	−38.20	−7.20	−72.00	−65.00	−7.00
m-Methylbenzoic acid	−42.10	−38.20	−3.90	−68.70	−65.00	−3.70
p-Methylbenzoic acid	−43.60	−38.20	−5.40	−70.20	−65.00	−5.20
2,6-Dimethylbenzoic acid	−45.10	−38.20	−6.90	−71.70	−65.00	−6.70
3,5-Dimethylbenzoic acid	−42.40	−38.20	−4.20	−69.00	−65.00	−4.00
2,3,4-Trimethylbenzoic acid	−43.30	−38.20	−5.10	−69.90	−65.00	−4.90
2,4,6-Trimethylbenzoic acid	−44.80	−38.20	−6.6	−71.40	−65.00	−6.40
3,4,5-Trimethylbenzoic acid	−42.60	−38.20	−4.4	−69.00	−65.00	−4.00

$\Delta = \Delta K'_{mol} - \Delta K'_{benzene}$ and $\Delta = \Delta K_{semi} - \Delta K_{calcd}$.

and $\Delta K_{semi} = -69.60 \times 10^{-6}$ emu mol^{-1}. The observed magnetic data of this compound (in 10^{-6} emu mol^{-1}) as previously obtained by the author[16-18] are:

$K_1 = -48.09$, $K_2 = -46.09$, $K_3 = -117.32$,

$(1/2)(K_1+K_2)_{obsd} = -47.53$ and $\Delta K = -69.79$

It is clear that the values of $(1/2)(K_1+K_2)_{obsd}$ and that calculated according to Eq. 2 are identical. This can be regarded as a check on the accuracy of this method. It is of interest to correlate the magnetic data of these molecules with their hydrogen-bonding systems.

In the crystalline state, these compounds are strongly hydrogen-bonded. The main feature of the crystal structure of the acid molecules is that, each two molecules are associated by intermolecular hydrogen bonding to form dimer. The carboxyl groups of the two molecules and the hydrogen bonds form an 8-membered ring. In recent years much attention has been paid to study the effect of hydrogen bonding on the magnetic properties of aromatic compounds.

Preliminary results on a general investigation of diamagnetism and hydrogen bonding were discussed by Rumpf and Seguin.[35] They used Pascal-Pacault method for the calculation of the mean susceptibility χ_M^{calcd} of some aromatic molecules associated with hydrogen bonds. Upon comparing the calculated value of χ_M^{calcd} of a given molecule with its observed one, a lowering was observed. They attributed this small difference between the calculated and the observed values of χ_M to the effect of the hydrogen bonding. The application of this method on the compounds under investigation is shown in Table 1. The small difference $\Delta\chi_M$ between χ_M^{calcd} and χ_M^{obsd} may be due to the contribution of the intermolecular hydrogen bonding of these molecules. This conclusion was confirmed recently by Haberditzl[36] on a similar work, who observed that a change in diamagnetism of 1—5% is obtained on the formation of the hydrogen bonds.

According to Lonsdale,[37] any satisfactory study of the effect of the hydrogen bonds on diamagnetism must take into account the three principal susceptibilities (K_1, K_2, and K_3) of the molecule. Furthermore, Mason[38] showed that the hydrogen bond can give rise to electron delocalization resulting in magnetic anisotropy. The effective delocalization term $\Delta K'$ as given by Mason, Davies,[12] and by Craig[39] is

$$\Delta K' = K_3 - \Sigma\chi_{atomic}.$$

Constitutive corrections are not used.[10] For benzene ring, $K_3 = -94.60 \times 10^{-6}$ emu mol^{-1} [40] and $\Sigma\chi_{atomic} = -56.40 \times 10^{-6}$ emu mol^{-1}, thus the value of $\Delta K'$ is -38.20×10^{-6} emu mol^{-1}. This value of $\Delta K'$ for benzene ring is in agreement with a value of -37.80×10^{-6} emu mol^{-1} as calculated recently by Edwards and McWeeny.[9] The values of the effective delocalization term of each compound are shown in Table 3. As can be seen from Table 3, the value of $\Delta K'$ of each molecule of the eight compounds is numerically higher than that of the benzene ring. This may be due to the additional delocalization resulting from the intermolecular hydrogen bonding of these molecules as suggested by Mason.

The contribution of the hydrogen bonding on the magnetic anisotropy of the molecule may also be investigated by comparing the semiexperimental magnetic anisotropy with the calculated one. The most recent calculated values of the magnetic anisotropy (in 10^{-6} emu mol^{-1}) of the benzene ring are: −60.90,[6] −58.61,[8] −60.24,[22] and 60.00.[23] Its observed that magnetic anisotropy is −59.70.[40] The magnetic anisotropy of the benzene ring is taken as −60.00 through this paper. The magnetic anisotropy of the COOH group is -5×10^{-6} emu mol^{-1}.[20] The CH_3 group or (groups) is or (are) assumed to be magnetically isotropic. Thus the magnetic anisotropy of any acid molecule is -65×10^{-6} emu mol^{-1}. The difference between the semiexperimental anisotropy and the calculated one is taken as the effect of the hydrogen bonding.

From Table 3, it is clear that the numerical increase in the semiexperimental magnetic anisotropy over the calculated one for one molecule is about -5×10^{-6} emu mol^{-1}. Thus for one dimer (two molecules), this contribution is about -10×10^{-6} emu mol^{-1}. Referring to the crystal structures, this value is ascribed to the magnetic anisotropy of an 8-membered ring formed by the two hydrogen bonds linking the two molecules of the dimer.

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