© 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 586—589 (1990) [Vol. 63, No. 2

Magnetic Studies of Some Benzamide Derivatives

M. M. Abdel-Kader
Physics Department, Faculty of Science, Cairo University, Giza, Egypt

(Received June 6, 1989)

The diamagnetic susceptibilities of benzamide, methylbenzamides, and hydroxybenzamides have been accurately measured. From these measurements and the calculated values of the in-plane susceptibilities, the semi-experimental anisotropies have been obtained. The magnetic data are correlated with the arrangement of these molecules in the crystals.

Aromatic hydrocarbons are characterized by strong magnetic anisotropy. The principal molecular susceptibility K_3 (normal to the plane of the ring) is greater than the principal susceptibilities K_1 and K_2 (in the plane of the ring). This is usually interpreted in terms of "ring currents" involving the motion of mobile π-electrons around cyclic interatomic paths.[1,2] The contribution of the ring current to the magnetic properties of aromatic molecules has been calculated recently by several authors.[3–8] An interesting discussion on the use of ring current concept has been also given by Gomes.[9] The contribution of the σ-electrons and the local effect to the anisotropies of benzene and other systems were also investigated.[10,11]

Hoarau[12] suggested that the London anisotropy probably accounts for not more than half of the observed anisotropy of benzene, and the rest is due to the anisotropies of localized σ-electrons and π-electrons according to the equation:

$$\Delta K_{\mathrm{obs}}=\Delta K_{\mathrm{London}}+\Delta K_{\sigma}+n\sum K_{\pi} \qquad (1)$$

O'Sullivan and Hameka[13] reported that the susceptibility can be represented as a sum of three terms, namely the contribution from the σ-electrons and that from the π-electrons and the contribution from σ–π interactions.

The principal molecular susceptibilities K_1, K_2, and K_3, where K_1, K_2 are the in-plane susceptibilities and K_3 (or $K^{\perp}$) is the out-of-plane susceptibility, can be estimated by measuring the crystal susceptibilities (χ_1, χ_2, and χ_3) along its principal axes combined with the orientation of the molecule in the crystal. The mathematical relations concerning the transition from the crystal susceptibilities (χ_1, χ_2, and χ_3) to molecular susceptibilities (K_1, K_2, and K_3) have been given by Lonsdale and Krishnan.[14] Many investigations for aromatic hydrocarbons have been made in this way.[15–17] One of the main disadvantages of this method is that, the accuracy of measurements depends on the success of obtaining large single crystal, and the detailed X-ray structures should be also known.

Akamatu and Matsunaga[18] calculated the values of the in-plane and out-of-plane susceptibilities for a number of aromatic hydrocarbons from the measured values of the mean molar susceptibilities. In recent series of papers,[6,19] Blustin uses a localized π-bond model with a success of calculating both the magnetic susceptibilities and chemical shifts of a variety of benzenoid hydrocarbons.

In the present work, the anisotropy of the molecule has been calculated semi-experimentally. According to Hoarau,[12] the value of the in-plane susceptibility is given by

$$K^{\parallel}=\frac{1}{2}(K_1+K_2)=\sum\chi_{\mathrm{A}}+n\alpha \qquad (2)$$

where n is the number of trigonally hybridized carbon atoms and α is a constitutive correction ($\alpha=3.8\times10^{-6}$ emu mol^{-1}) expressing quantitatively the effect of ΔK_{π} of Eq. 1 on the in-plane susceptibilities. Since, the magnetic anisotropy ΔK of the molecule is defind as:

$$\Delta K=K_3-\frac{1}{2}(K_1+K_2)=K^{\perp}-K^{\parallel},$$

and

$$\chi_{\mathrm{M}}^{\mathrm{obs}}=\frac{2K^{\parallel}+K^{\perp}}{3}$$

therefore

$$\Delta K_{\mathrm{semi}}=3\,(\chi_{\mathrm{M}}^{\mathrm{obs}}-K^{\parallel}) \qquad (3)$$

According to Akamatu and Matsunaga,[18] the anisotropic part of the ΔK is mainly due to the circulation of the π-electrons in the plane of molecule, whereas K_1 and K_2 or $1/2\ (K_1+K_2)$ is the isotropic part and will be the sum of the atomic susceptibilities based on the distribution of electrons being spherically symmetric. Thus we have

$$K^{\parallel}=\sum\chi^{\parallel}(\mathrm{AV}) \qquad (4)$$

where $\chi^{\parallel}(\mathrm{AV})$ is the average of the two principal components of the susceptibility when the field is in plane. Equation 4 has been used by Mason[20] and by Amos et al.[3] for the calculations of the in-plane susceptibilities of some aromatic compounds. In this paper, the values of the in-plane susceptibilities have been calculated according to Eqs. 2 and 4 and the average is taken. This seems to us more accurate.

In previous work,[16,17] we have studied the effect of the inter- and intramolecular hydrogen bonds to the magnetic anisotropies of some aromatic molecules experimentally. Recently, we have also studied semi-experimentally some aromatic molecules.[21,22]

Experimental

The compounds studied in the paper are: Benzamide, *o*-methylbenzamide, *m*-methylbenzamide, *p*-methylbenzamide, *o*-hydroxybenzamide, *m*-hydroxybenzamide, and *p*-hydroxybenzamide. The crystal structures of these compounds are known[23–28] except for the last compound.

The Gouy method was used for the measurements of the mean molar susceptibility, χ_M^{obs} of each compound. In this method, the purified material was finely powdered and was uniformly packed in the specimen tube. The effect of the container was taken into account. The accuracy of the balance amounts to 10^{-5} g m. A correction for the porosity of the packed powder was applied. Since good powdering and packing were followed, random orientation might be assumed. Thus the results obtained from adopting such a procedure gave consistent diamagnetic susceptibility values.

Results and Discussion

The observed and the calculated molar susceptibilities, χ_M^{obs} and χ_M^{calc} for each compound are listed in Table 1. The method used for the calculation of χ_M^{calc} is as follows (the numerical values are in the units of 10^{-6} emu mol^{-1} in the follwing):

a. The mean molar susceptibility of the benzene ring is taken as −55.20.[3]

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 diamagnetic susceptibility of the $(CONH_2)^+$ is taken as −17.10.[29] Accordingly, the diamagnetic susceptibility of the neutral $CONH_2$ is −(17.10+2.44)=−19.54.

Table 1. Observed and Calculated Susceptibilities

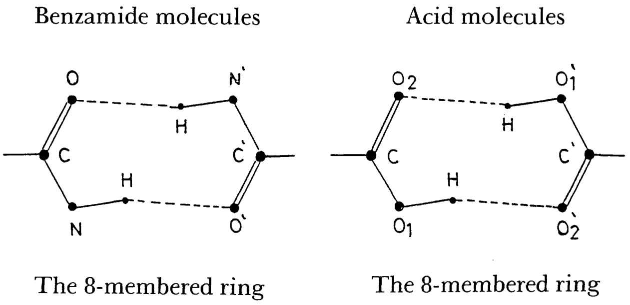
Compound	$10^6\chi_M^{obs}$/ emu mol^{-1}	$10^6\chi_M^{calc}$/ emu mol^{-1}	$\Delta\chi_M$
Benzamide	−73.40	−72.74	−0.66
o-Methylbenzamide	−83.34	−83.96	+0.62
m-Methylbenzamide	−83.71	−83.96	+0.25
p-Methylbenzamide	−83.39	−83.96	+0.57
o-Hydroxybenzamide	−77.63	−77.44	−0.19
m-Hydroxybenzamide	−78.20	−77.44	−0.76
p-Hydroxybenzamide	−77.81	−77.44	−0.37

Multiplying each value of χ_M, $\Delta\chi$, K, and ΔK in emu mol^{-1} by 4π gives those in cm^3 ml^{-1} of the SI units.

d. The mean molar susceptibility of the CH_3 group is −13.22.[30] The mean molar susceptibility for the OH group is −6.70.[31] Thus for benzamide, χ_M^{calc} is: (−55.20+2−19.54)=−72.74, which is in agreement with a value of −71.90 given in Ref. 29.

The slight differences in χ_M^{obs} of the methylbenzamide molecules can be explained in terms of the positional isomerism of the CH_3 group. The $CONH_2$ group is *m*-directing. On the other hand, the CH_3 is *o*,*p*-directing.[32] Thus the order of magnitude of the χ_M^{obs} values should be *m*>*p*>*o*.[33] This is seen to be so. However, these difference in χ_M^{obs} are small to be significant. This is to be expected, since $CONH_2$ is not strong *m*-directing[21a] and the CH_3 and/or the OH groups are *o*,*p*-directing groups.[32,33]

The compounds under investigations are strongly hydrogen bonded in their crystalline states. The molecular packing modes of primary amides and the hydrogen bonded contacts of amide groups have been considered by Leiserowitz and Schmidt.[34] Accordingly, the majority of amides form centrosymmetric hydrogen-bonded pair, the centers of which coincide with centers of symmetry of the unit cell. For benzamide molecules[23] the hydrogen bonding system consists of centrosymmetric pairs linked side by side to other pairs, which are b-translation related. Infinite ribbons, two molecule wide, therefore extend along the b-direction with the width of ribbon roughly in the c-direction.[23] In Fig. 1 the 8-membered centrosymmetric hydrogen bonded ring formed within the dimer together with that formed by the two COOH groups (for comparison) are shown.



Benzamide molecules — The 8-membered ring

Acid molecules — The 8-membered ring

Fig. 1.

Table 2. The Principal Molecular Susceptibilities (in 10^{-6} emu mol^{-1})

Compound	$\Sigma\chi_A$	$\frac{1}{2}(K_1+K_2)$ $=\Sigma\chi_A+n\alpha$	$\frac{1}{2}(K_1+K_2)$ $=\Sigma\chi^{\parallel}$(AV)	$\frac{1}{2}(K_1+K_2)$ mean $K^{\parallel}$	K_3 or $K^{\perp}$
Benzene	−56.40	−33.60	−35.52	−34.56	−95.46
Benzamide	−77.70	−51.10	−49.94	−50.52	−119.16
o-Methylbenzamide	−89.10	−62.50	−58.55	−60.52	−128.98
m-Methylbenzamide	−89.10	−62.50	−58.55	−60.52	−130.09
p-Methylbenzamide	−89.10	−62.50	−58.55	−60.52	−129.13
o-Hydroxybenzamide	−82.30	−55.70	−53.48	−54.59	−123.71
m-Hydroxybenzamide	−82.30	−55.70	−53.48	−54.59	−125.42
p-Hydroxybenzamide	−82.30	−55.70	−53.48	−54.59	−124.25

Table 3. The Contribution of Hydrogen Bonding (in 10^{-6} emu mol^{-1})

Compound	$\Delta K'=K_3-\sum\chi_A$	ΔK_{semi}	ΔK_{calc}	Δ	Hydrogen bond distances/Å Within a dimer	Hydrogen bond distances/Å Between dimers
Benzene	−39.06	−60.9	—	—	—	—
Benzamide	−41.46	−68.64	−64.05	−4.59	2.933	2.907
o-Methylbenzamide	−39.88	−68.46	−64.05	−4.41	3.001	2.859
m-Methylbenzamide	−40.99	−69.57	−64.05	−5.52	3.220	2.970
p-Methylbenzamide	−40.03	−68.61	−64.05	−4.56	2.968	3.013
o-Hydroxybenzamide	−41.41	−69.12	−64.05	−5.07	2.76	2.98
m-Hydroxybenzamide	−43.12	−70.83	−64.05	−6.78	2.94	2.94, 2.98
p-Hydroxybenzamide	−41.95	−69.66	−64.04	−5.61	—	—

The planarity of the last ring and its contribution to the magnetic anisotropy of the acid molecules have been discussed.[16,17,21,22] For the methylbenzamide molecules similar hydrogen bonding systems are observed. For the hydroxybenzamide compounds, the OH group participate in the hydrogen bonding systems. Thus for the *o*-hydroxybenzamide, the molecules are connected by two N-H···O hydrogen bonds, the first set forming a dimer across the center of symmetry and the second set, joining such dimers into an endless chain extended along the a-axis. For the *m*-hydroxybenzamide, there are three types of hydrogen bonds.[28] The reference molecule at (x, y, z) is connected by the first set of O-H···O (amide) with the molecule at ($1-x$, $1-y$, $1-z$) to form a molecular pair across the center of symmetry. The pairs are piled up infinitely along the b-axis by second set of N-H···O (amide). The third hydrogen bonds, N-H···O (hydroxy), join the neighboring piles which is related to each other by the screw axis. A summary of the hydrogen bond lengths is given in Table 3.

It is of interest to correlate the magnetic data of these compounds with their hydrogen bonding systems. The first report on the diamagnetism and the hydrogen bonding was first observed by Angus and Hill.[35] Rumpf and Segun[36] used the Pascal-Pacault method for the determination of χ_M^{calc} and compared it with χ_M^{obs} for certain hydrogen bonded molecules; a lowering was observed which they attributed to the contribution of the hydrogen bonding of the molecule. A change in diamagnetism of 1—5% was observed by Haberditzal[8] with the formation of the hydrogen bonding.

Lonsdale[37] suggested that 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. The value of 1/2 (K_1+K_2) and the out-of-plane susceptibility, K_3 for the compounds are given in Table 3. The magnetic data for the benzene ring are also included for comparison. The effect of the hydrogen bonding on the anisotropy of the molecule can be investigated by comparing the delocalization anisotropy of the molecule by that of the benzene ring. According to Mason[20] the hydrogen bond can give rise to electron delocalization resulting in magnetic anisotropy. The delocalization anisotropy $\Delta K'$ is given by

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

The atomic susceptibilities used in the calculation of $\sum\chi_{\text{atomic}}$ are: $\chi_C=-7.4$ and $\chi_H=2.0$, given by Mason[20] and $\chi_O=-4.6$.[38] For the χ_N, we have two different values, −9.0[20] and −5.6,[38] thus the mean of these two values is taken, i.e. $\chi_N=-7.30$. On the other hand, the average susceptibilities $\chi^{\parallel}$(AV) used for the calculation of $K^{\parallel}$ are:

$$\chi_C^{\parallel}(\text{AV})=-3.23,^{3)}\ \chi_H^{\parallel}(\text{AV})=-2.69,^{3)}$$

$$\chi_O^{\parallel}(\text{AV})=-3.45,^{39)}\ \chi_N^{\parallel}(\text{AV})=-4.00,^{20)}$$

$$\chi_{=O}^{\parallel}(\text{AV})=-4.50.^{20)}$$

The values of $\Delta K'$ of the molecules are given in Table 3. For the benzene ring, the value most recently calculated is −37.80.[6] The experimental value of this term is −38.20.[40] The method used in this work yields the value of −39.06. It can be seen from Table 3 that the value of any benzamide molecule is numerically greater than that of the benzene ring. This additional anisotropy of the molecule is attributable to the effect of the electron delocalization resulting from the hydrogen bonding as suggested by Mason.[20]

One can investigate the effect of the hydrogen bonding to the magnetic anisotropy of a given molecule by comparing the semi-experimental anisotropy ΔK_{semi} of that molecule with the calculated value, ΔK_{calc}. The difference between them may be taken as the contribution of the hydrogen bond. The magnetic anisotropy of the benzene ring has been extensively considered both theoretically and experimentally.[3,4,7] The average value of this anisotropy is about −60. The method used in this paper yields the value of −60.90 as given in Table 3. The magnetic anisotropy of the C=O group is 3.15.[15] The OH and the CH_3 groups are assumed to be magnetically isotropic.

Thus the anisotropy of one molecule without any contribution of hydrogen bonding is about −64.05. The difference between the semi-experimental anisotropy of one molecule and that value is taken as the effect of the hydrogen bonding on its anisotropy.

From the data shown in Table 3 it is clear that the values ΔK_{semi} are numerically higher than the calculated one (i.e. 64.05). The average increase in the anisotropy of one molecule of methylbenzamides (and/or benzamide) is about 4.77. Thus the combined effect of two molecules (i.e. one dimer) is therefore 9.54. Referring to the structures of these molecules, this value 9.54 is ascribed to the magnetic anisotropy of the 8-membered ring (Fig. 1) formed by two hydrogen bonding of these molecules.

On the other hand, the corresponding increase in the anisotropy of one molecule of hydroxybenzamides is about 5.82. Thus for two molecules (one dimer) this value is 11.64, which is slightly higher than that of methylbenzamide dimer. This is very interesting because for hydroxybenzamide dimer we have beside the 8-membered ring formed by intermolecular hydrogen bond, there is a 6-membered ring resulting from the intramolecular hydrogen bonds i.e. the OH groups are participated in the hydrogen bonding systems.[27,28] In other words, we have stronger hydrogen bond and hence high (numerically) magnetic anisotropy. The results of hydroxybenzamides shown in Table 3 confirm this conclusion.

References

1) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

2) F. London, *J. Phys. Rad.*, **8**, 397 (1937).

3) A. T. Amos and F. Roberts, *J. Chem. Phys.*, **50**, 2375 (1969).

4) P. Lazzeretti and F. Taddei, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1825 (1972).

5) H. Haberditzel, *Angew. Chem., Int. Ed. Engl.*, **5**, 288 (1966).

6) T. G. Edwards and R. McWeeny, *Chem. Phys. Lett.*, **10**, 283 (1971).

7) P. H. Blustin, *Mol. Phys.*, **36**, 297 (1978).

8) J. Nowakowski, *Theor. Chim. Acta*, **10**, 79 (1968).

9) J. A. N. F. Gomes, *Mol. Phys.*, **40**, 765 (1980).

10) J. A. Pople, *J. Chem. Phys.*, **41**, 2559 (1964).

11) J. I. Musher, *J. Chem. Phys.*, **13**, 4081 (1965).

12) J. Hoarau, *Ann. Chim.*, **13**, 544 (1956).

13) P. S. O'Sullivan and H. F. Hameka, *J. Am. Chem. Soc.*, **92**, 1821 (1970).

14) K. Lonsdale and K. S. Krishnan, *Proc. R. Soc. London, Ser. A*, **156**, 597 (1936).

15) M. A. Lasheen, *Phil. Trans. R. Soc. London, Ser. A*, **256**, 357 (1964), *Acta Crystallogr., Sect. A*, **24**, 289 (1968).

16) S. M. Salem, S. A. Abdel-Hadi, and M. M. Abdel-Kader, *Z. Phys. Chem., Leipzig*, **257**, 641 (1976).

17) a) M. M. Abdel-Kader, *Chem. Phys. Lett.*, **93**, 297 (1982); b) M. M. Abdel-Kader, M. Sc. Thesis, Cairo University (1974); c) M. M. Abdel-Kader, *Acta Phys. Polonica*, **A63**, 539 (1983); d) M. M. Abdel-Kader, *Mol. Phys.*, **48**, 1145 (1983).

18) H. Akamatu and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **26**, 364 (1953), **29**, 800 (1956).

19) P. H. Blustin, *Mol. Phys.*, **36**, 1441 (1978); *Chem. Phys. Lett.*, **64**, 507 (1979).

20) R. Mason, *Mol. Phys.*, **4**, 191 (1961).

21) a) M. M. Abdel-Kader, *Acta Phys. Polonica*, **A64**, 595 (1983); **A65**, 263 (1984); b) M. M. Abdel-Kader, *Bull. Chem. Soc. Jpn.*, **55**, 3134 (1983).

22) M. M. Abdel-Kader and Z. E. Kandeel, *Indian J. Chem., Sect. A*, **22**, 1945 (1983).

23) C. F. Blake and R. W. Small, *Acta Crystallogr., Sect. B*, **28**, 220 (1972).

24) Y. Kato, M. Yamazaki, and M. Yokota, *Mem. Osaka Kyoiku Univ. Ser. III*, **27**, 125 (1979).

25) S. Orii, T. Nakamara, Y. Takai, Y. Sasada, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **36**, 788 (1963).

26) Y. Kato, N. Oguro, R. Tanaka, M. Tadeishi, and M. Hirata, *Mem. Osaka Kyoiku Univ. Ser. III*, **1981**, 2991.

27) Y. Sasada, T. Takano, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **37**, 940 (1964).

28) Y. Katsube, Y. Sasada, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **39**, 2576 (1966).

29) Tai-Yuan Yang, *J. Chem. Phys.*, **16**, 865 (1948).

30) V. C. G. Trew, *Trans. Faraday Soc.*, **49**, 604 (1953).

31) C. M. French, *Trans. Faraday Soc.*, **50**, 1320 (1954).

32) S. Sriraman and R. Sabesan, *Trans. Faraday Soc.*, **58**, 1080 (1962).

33) A. Balih and M. Mohamed, *Indian J. Chem.*, **9**, 963 (1971).

34) L. Leiserowitz and M. J. Schmidt, *J. Chem. Soc. A*, **1969**, 2372.

35) W. Angus and W. Hill, *Trans. Faraday Soc.*, **1940**, 923.

36) P. Rumpf and M. Seguin, *Bull. Soc. Chim. Fr., D*, **1949**, 366 .

37) K. Lonsdale, *Trans. Faraday Soc.*, **36**, 927 (1940).

38) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York (1962), p. 60.

39) J. A. Pople, *J. Chem. Phys.*, **37**, 609 (1961).

40) D. W. Davies, *Nature (London)*, **190**, 1102 (1961).