Diamagnetic susceptibilities of some substituted anisoles and thio-anisoles. Evidence for steric enhancement of resonance

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Abstract. Evidence for steric enhancement of resonance in some benzene derivatives is obtained from their diamagnetic susceptibilities. Conjugative interaction of substituents in the benzene ring results in a decrease in diamagnetic susceptibility. For 2-methyl-4-nitroanisole and 2-halogeno-4-nitroanisoles the observed diamagnetic susceptibilities are significantly lower than the expected value, indicating that the 2-substituent in these compounds enhances the resonance interaction of the 1,4-substituents. Interestingly, the diamagnetic susceptibility data also show steric inhibition of resonance in 2,6-disubstituted-4-nitroanisoles. 2-Methyl-4-nitrothioanisole seems to exhibit a behaviour similar to that of its oxygen analogue, though the evidence for steric enhancement of resonance in this case is not beyond doubt. 2,6-Dimethyl-4-nitrothioanisole, however, convincingly shows the expected steric inhibition of resonance. The diamagnetic susceptibilities of 3-substituted-4-methoxyacetophenones also furnish further evidence for steric enhancement of resonance.

Keywords. Diamagnetic susceptibilities; 4-nitroanisoles; 4-nitrothioanisoles; 4-methoxy-acetophenones; steric enhancement of resonance; steric inhibition of resonance.

1. Introduction

After the discovery of steric enhancement of resonance (Baliah and Uma 1960), several studies have afforded additional evidence for the phenomenon (Krishna Pillay and Kanagavel 1976; Baliah and Kanagasabapathy 1978; Baliah and Theymoli 1978; Ganapathy and Jayagandhi 1979; Baliah and Satyanarayana 1980, 1985; Ganapathy *et al* 1981; Uma and Kalavathi 1982; Baliah and Sundari 1983). In the present investigation, evidence for steric enhancement of resonance has been obtained from diamagnetic susceptibilities of some benzene derivatives.

2. Experimental

2.1 *Materials*

The compounds used were either obtained commercially and then highly purified or prepared as described in the literature. The purity of all the compounds was tested by g.l.c.

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2-Methyl-4-nitroanisole, m.p. 64°; 2,6-dimethyl-4-nitroanisole, m.p. 91°; 2,6-dichloroanisole, b.p. 105–106°/20 mm; 2-chloro-4-nitroanisole, m.p. 98°; 2,6-dichloro-4-nitroanisole, m.p. 99°; 2-methyl-4-nitrothioanisole, m.p. 79°; 2,6-dimethyl-4-nitrothioanisole, m.p. 85°; 2-methylthioanisole, b.p. 96–97/16 mm; 2,6-dimethylthioanisole, b.p. 80°/13 mm; 3-methyl-4-methoxyacetophenone, b.p. 129–130°/10 mm; 3,5-dimethyl-4-methoxyacetophenone, b.p. 134°/11 mm; 3-chloro-4-methoxyacetophenone, m.p. 80°; 3-bromo-4-methoxyacetophenone, m.p. 87°.

2.2 *Apparatus*

The magnet employed was a large one from Newport Instruments, England. The pole faces used were 3 cm in diameter and the air gap had a width of 1·2 cm. The current for the electromagnet was supplied by a 110-volt direct current generator. With the aid of rheostats, the current in the circuit could be adjusted to 5, 6 or 7 amperes. The magnetic field strength in this current range varied from about 14,000–18,000 oersteds. The balance was mounted on a platform, one metre above the electromagnet to avoid any direct influence resulting from the magnetic field on any part of the balance.

2.3 *Measurements*

The magnetic susceptibilities were determined by means of a modified Gouy method. The temperature was kept nearly constant (27–28°) during the measurements. The Gouy tube was made of pyrex glass with a ground glass stopper and was suspended by a fine copper wire from the centre of the left pan of the balance. Three tubes each of length 11 cm and diameter 0·97, 0·86 and 0·66 cm, respectively, were used. For each tube, measurements were taken at three different magnetic fields corresponding to current strengths of 5, 6 and 7 A. Hence, using three tubes and three field strengths, nine readings could be taken for a liquid or solution.

The volume susceptibility, κ, of air was taken to be $+0·0300 \times 10^{-6}$ emu (Michaelis 1949) at the temperature of measurement. The volume susceptibility of benzene was obtained by multiplying the specific susceptibility of benzene by its density. Let W_1 be the weight of the empty tube at zero field strength and W_2 at constant field strength. Let W_3 and W_4 be the weights of tube with benzene without the magnetic field and with the field, respectively. Let W_5 and W_6 be the weights of tube with substance (solution) without and with the field, respectively. Then,

$$(\kappa_{\text{benzene}} - \kappa_{\text{air}}) \propto (W_3 - W_4) - (W_1 - W_2),$$

$$\Delta\kappa_{\text{b}-\text{a}} \propto W_{3,4-1,2}, \tag{1}$$

$$(\kappa_{\text{substance}} - \kappa_{\text{air}}) - (\kappa_{\text{benzene}} - \kappa_{\text{air}}) \propto$$

$$[(W_5 - W_6) - (W_1 - W_2)] - [(W_3 - W_2) - (W_1 - W_2)],$$

$$\therefore (\kappa_{\text{substance}} - \kappa_{\text{benzene}}) \propto (W_5 - W_6) - (W_3 - W_4)$$

$$\kappa_{\text{s}-\text{b}} \propto \Delta W_{5,6-3,4}. \tag{2}$$

From equations (1) and (2), κ_{s-b} can be evaluated. Hence $\kappa_{\text{substance}} = \kappa_{\text{benzene}} + \kappa_{s-b}$, and specific susceptibility, $\chi = \kappa_{\text{substance}}/\text{density}$. If the substance was liquid, the Gouy tube was filled with the pure liquid and measurements were made. But with solids, the susceptibilities were determined in benzene solution (nonpolar solvent). In a couple of cases, however, dioxane was used as solvent due to the low solubility of the solutes in benzene. The susceptibility of the solute can be obtained from the susceptibility of the solution by Wiedemann's additivity law (Selwood 1956):

$$\chi_{12} = \chi_1 W_1 + \chi_2 W_2,$$

where χ_{12}, χ_1 and χ_2 are the specific susceptibilities of the solution, solvent and solute, respectively; W_1 and W_2 are the weight fractions of the solvent and solute, respectively.

In the case of liquids the density was determined using a 1 ml pyknometer. A 10 ml specific gravity bottle was used for measuring the densities of solutions.

Before commencing measurements on solutions, the susceptibilities of a few liquids, whose susceptibilities were determined in the liquid state, were also determined in solution in benzene or dioxane. The susceptibilities obtained in the solution state and in the liquid state were found to agree within experimental error. Thus, only after making sure that the compounds under investigation did not exhibit significant magnetic susceptibility changes when dissolved in benzene or dioxane (due to solute-solvent interaction), were measurements in solution made.

3. Results and discussion

Table 1 gives the specific and molar susceptibilities of the compounds examined in the present study; χ refers to the specific susceptibility and χ_M to the molar susceptibility. The specific and molar susceptibilities are given in units of -10^{-6} emu.

Conjugative interaction of substituents in the benzene ring results in a decrease in diamagnetic susceptibility. Thus, of the three isomeric nitroanilines, the para isomer has the lowest diamagnetic susceptibility (Baddar and Sugden 1950). The lower diamagnetic susceptibility of p-nitroaniline was attributed to the strong conjugative interaction of the substituent groups. This view was also supported by others (Mikhail 1953; Baliah and Srinivasan 1971). The magnetic susceptibility of p-nitroaniline was found to be 66·8 while the value calculated from atomic susceptibilities and structural terms (Ingold 1953) comes to 68·9, the difference being as much as 2·1. The difference for the meta isomer is almost nil (observed value, 69·0, and calculated value, 68·9) there being no conjugative interaction of the substituent groups.

The postulate of steric enhancement of resonance in a compound like 2-methyl-4-nitroanisole attributes increased resonance interaction of the para substituents to the presence of the methyl group in the position ortho to the methoxyl. The methyl group makes the methoxyl orient away from itself (I) and facilitates its becoming planar with the benzene ring to a greater extent. In the absence of the ortho-methyl group the methoxyl has greater freedom to rotate and its chances of becoming coplanar with the benzene ring will be less. The planarity of

Table 1. Magnetic susceptibility data*.

Compound	χ	χ_M
Anisole	0·6595 ± 0·0005	71·2
4-Nitroanisole	0·5051 ± 0·0008	77·3
2-Methylanisole	0·6815 ± 0·0007	83·1
2-Methyl-4-nitroanisole	0·5307 ± 0·0008	88·7
2,6-Dimethyl-4-nitroanisole	0·5555 ± 0·0013	100·6
2,6-Dimethylanisole	0·6880 ± 0·0010	93·6
2-Chloroanisole	0·6134 ± 0·0008	87·4
2-Chloro-4-nitroanisole	0·4954 ± 0·0009	92·9
2,6-Dichloro-4-nitroanisole	0·4939 ± 0·0011	109·6
2,6-Dichloroanisole	0·5790 ± 0·0015	102·5
Thioanisole	0·6676 ± 0·0009	82·8
4-Nitrothioanisole	0·5220 ± 0·0014	88·2
2-Methylthioanisole	0·6928 ± 0·0011	95·6
2-Methyl-4-nitrothioanisole	0·5505 ± 0·0012	100·8
2,6-Dimethylthioanisole	0·6943 ± 0·0010	105·5
2,6-Dimethyl-4-nitrothoanisole	0·5710 ± 0·0015	112·5
Acetophenone	0·6013 ± 0·0003	72·2
4-Methoxyacetophenone	0·5855 ± 0·0010	87·8
3-Methyl-4-methoxyacetophenone	0·6047 ± 0·0006	99·2
3,5-Dimethyl-4-methoxyacetophenone	0·6218 ± 0·0006	100·7
3-Chloro-4-methoxyacetophenone[D]	0·5603 ± 0·0008	103·4
2-Bromoanisole	0·5162 ± 0·0005	96·5
3-Bromo-4-methoxyacetophenone[D]	0·4910 ± 0·0021	112·3

* For solids the solvent used was benzene and only in two cases (indi-
cated by D) dioxane was used. In the case of liquids, they were used
as such.

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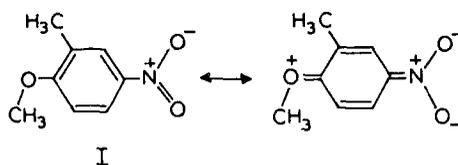
the groups being essential for their resonance interaction, there should be greater resonance in 2-methyl-4-nitroanisole than in 4-nitroanisole. This should be reflected in their diamagnetic susceptibilities, the former having a lower value than the latter. The data given in tables 2 and 3 reveal the expected order.

The diamagnetic susceptibilities of benzene and nitrobenzene are 54·8 and 61·8, respectively. The replacement of an H atom in benzene by an $-NO_2$ group thus increases the value by 7·0. For a similar replacement of the para H atom in anisole by $-NO_2$, the increase is only 6·1. This lowering is the result of conjugative interaction of the nitro and methoxy groups. In the case of 2-methyl-4-nitroanisole the difference is even lesser (5·8), indicating greater conjugation of the nitro and methoxy groups. Hence there is steric enhancement of resonance. This view is strengthened by the fact that for 2,6-dimethyl-4-nitroanisole, in which resonance is inhibited by the two methyl groups flanking the methoxyl, the difference is 7·0 which is indicative of steric suppression of resonance by the two methyl groups. The other compounds given in table 1 also show that steric enhancement of resonance

Table 2. The influence of substituents, ortho to the methoxyl, on the diamagnetic susceptibilities of 4-nitroanisoles and 4-nitrothioanisoles.

Nitro compound	χ_M (observed)	Reference compound	χ_M (observed)	Difference due to the introduction of NO_2
Nitrobenzene	61·8*	Benzene	54·8*	+ 7·0
4-Nitroanisole	77·3	Anisole	71·2	+ 6·1
2-Methyl-4-nitroanisole	88·7	2-Methylanisole	83·1	+ 5·6
2-Chloro-4-nitroanisole	92·9	2-Chloroanisole	87·4	+ 5·5
2,6-Dimethyl-4-nitroanisole	100·6	2,6-Dimethylanisole	93·6	+ 7·0
2,6-Dichloro-4-nitroanisole	109·6	2,6-Dichloroanisole	102·5	+ 7·1
4-Nitrothioanisole	88·2	Thioanisole	82·8	+ 5·4
2-Methyl-4-nitrothioanisole	100·8	2-Methylthioanisole	95·6	+ 5·2
2,6-Dimethyl-4-nitrothioanisole	112·5	2,6-Dimethylthio-anisole	105·5	+ 7·0

* Baddar and Sugden (1950).

Table 3. The influence of substituents, ortho to the methoxyl, on the diamagnetic susceptibilities of 4-methoxyacetophenones.

Acetophenone	χ_M (observed)	Reference compound	χ_M (observed)	Difference due to the introduction of $-COCH_3$
Acetophenone	72·2	Benzene	54·8	+ 17·4
4-Methoxy	87·8	Anisole	71·2	+ 16·6
3-Methyl-4-methoxy	99·2	2-Methylanisole	83·1	+ 16·1
3-Chloro-4-methoxy	103·4	2-Chloroanisole	87·4	+ 16·0
3-Bromo-4-methoxy	112·3	2-Bromoanisole	96·5	+ 15·8
3,5-Dimethyl-4-methoxy	110·7	2,6-Dimethylanisole	93·6	+ 17·1

decreases and steric inhibition of resonance increases the diamagnetic susceptibility. The decrease for 2-chloro-4-nitroanisole is slightly more than that for 2-methyl-4-nitroanisole. This is presumably due to the greater bulk of chlorine compared to that of methyl, which increases the probability of the adjacent methoxyl attaining planarity with the benzene ring.

The nitrothioanisoles also show a similar trend but the fact that the difference for 2-methyl-4-nitrothioanisole is only 0·2 less than that for 4-nitrothioanisole indicates that steric enhancement of resonance in 2-methyl-4-nitrothioanisole, if at all it exists, is less than that in 2-methyl-4-nitroanisole. The value of 0·2 is near the range of experimental error and causes the above doubt. There is, however, no doubt in there being steric inhibition of resonance in 2,6-dimethyl-4-nitrothioanisole.

Table 3 shows the diamagnetic susceptibilities of 4-methoxyacetophenones. The nature of compounds given in this table is essentially the same as that given in table 2. The acetyl group is also an electron-attracting group like the nitro and so some 4-methoxyacetophenones were also included in the present study.

The replacement of H in benzene by $-COCH_3$ results in an increase of the diamagnetic susceptibility by 17·4. The difference between the magnetic susceptibi-

lities of 4-methoxyacetophenone and acetophenone is 16·6, indicating conjugative interaction of the CH_3O- and $-COCH_3$ groups in the former. The difference between the values for 3-methyl-4-methoxyacetophenone and 2-methylanisole is smaller (16·1) indicating steric enhancement of resonance in 3-methyl-4-methoxy-acetophenone. The difference in the case of 3,5-dimethyl-4-methoxyacetophenone is, however, high (17·1), indicating clearly steric inhibition of resonance in this compound. The data given for the chloro and bromo compounds further substantiate the conclusions so far drawn. It is of interest to note the difference between the magnetic susceptibilities of 3-bromo-4-methoxyacetophenone and 2-bromoanisole (15·8) is less than the difference between the values for 3-methyl-4-methoxyacetophenone and 2-methylanisole, indicating the greater influence of the bulkier bromine atom (compared to the methyl group) in enhancing the resonance interaction of the methoxy and acetyl groups.

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