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Magnetic susceptibilities of organic compounds: Part V—Influence of substituents on diamagnetic susceptibilities of disubstituted and trisubstituted benzenes

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The magnetic susceptibilities of a number of triads of isomeric disubstituted benzenes have been determined, choosing the compounds in such a way that the substituents are present in the following combinations: (i) two electron-releasing substituents, (ii) a halogeno and an electron-releasing substituent, (iii) a halogeno and an electron-attracting substituent, and (iv) two halogeno substituents. The data show that for types (i), (ii) and (iv), the *ortho* isomers have the highest magnetic susceptibilities, the susceptibilities decreasing in the order: *ortho* > *meta* > *para*; for type (iii), the *meta*-isomers have the highest susceptibilities, the susceptibilities decreasing in the order: *meta* > *para* > *ortho*. The diamagnetic susceptibilities of some isomeric trisubstituted benzenes have also been determined and the data reveal that the susceptibility is the highest where the crowding of substituents is the highest (1,2,3-isomer) and lowest where the substituents are staggered and least crowded (1,3,5-isomer). Another observation made in the case of trisubstituted benzene is the applicability of a principle of additivity of their diamagnetic susceptibilities.

In the present investigation the magnetic susceptibilities of a number of disubstituted and trisubstituted benzenes have been determined with a view to knowing the substituent effects. The disubstituted benzenes were so chosen as to contain (i) two electron-releasing substituents, (ii) a halogeno and an electron-releasing substituent, (iii) a halogeno and an electron-attracting substituent, and (iv) two halogeno substituents. The trisubstituted benzenes examined were the six isomeric dimethylphenols, the six isomeric dimethylanisoles, the three isomeric trichlorobenzenes and the three isomeric tribromobenzenes.

Materials and Methods

Wherever doubts existed, the purities of the liquid compounds were checked by VPC. Solids, both prepared in the laboratory and those available commercially were purified by repeated crystallisation.

The halogenotoluenes, dihalogenobenzenes and esters of halogenobenzoic acids were prepared as described in the literature. Chlorofluorobenzenes were prepared from the corresponding chloroanilines; *o*-chlorofluorobenzene, b.p. 139-40°; *m*-chlorofluorobenzene, b.p. 127°; and *p*-chlorofluorobenzene, b.p. 130°. Dimethylanisoles were prepared from the commercially available dimethylphenols; 2,3-dimethylanisole, b.p. 198-99°; 2,4-dimethylanisole, b.p. 191-92°; 2,6-dimethylanisole, b.p. 181-82°; 2,5-dimethylanisole, b.p. 194°; 3,4-dimethylanisole, b.p. 205°; and 3,5-dimethylanisole, b.p. 193°. The preparation of 1,2,3-trichlorbenzene involved the following steps: sulphanilamide → 3,5-dichlorosulphanilamide → 2,6-dichloroaniline → 1,2,3-trichlorobenzene, b.p. 218-19°, m.p. 53°. 1,2,4-Trichlorobenzene, b.p. 210°, was prepared as follows: *p*-dichlorobenzene → 1,4-dichloro-2-nitrobenzene → 2,5-dichloroaniline → 1,2,4-trichlorobenzene. 1,3,5-Trichlorobenzene, m.p. 63°, was prepared as follows: *p*-nitroaniline → 2,6-dichloro-4-nitroaniline → 3,5-dichloronitrobenzene → 3,5-dichloroaniline → 1,3,5-trichlorobenzene. The tribromobenzenes were prepared by adopting methods similar to those used for trichlorobenzenes; 1,2,3-tribromobenzene, m.p. 86-87°; 1,2,4-tribromobenzene, m.p. 44°; and 1,3,5-tribromobenzene, m.p. 120°.

Measurements and Calculation

The magnetic susceptibilities were determined by the Guoy method. Details of measurements and definition of symbols have been given in a previous paper[1]. To obtain the calculated susceptibilities, Ingold's values for atomic susceptibilities and structural terms[2], and the substitutent correction terms given by Baliah and Srinivasan[3] were used; in addition, the following substituents correction terms were

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used: OH, +0.7; COOH, +1.5; CN, +1.5; COOEt, −0.5.

Results and Discussion

The observed and calculated diamagnetic susceptibilities are given in Tables 1 and 2. Disubstituted benzenes are divided into four types: (i) compounds having both the substituents of the same kind, they being electron-releasing (in the case of cresols and anisidines, the two substituents are different, though both are electron-releasing); (ii) a halogen and an electron-releasing substituent; (iii) a halogen and an electron-attracting substituent; and (iv) two halogeno substituents. The halogeno-substituted compounds are particularly chosen because the electronic effects of halogens are not always easy to understand. The halogeno substituents exert electron-releasing mesomeric effect and electron-withdrawing inductive effect, both being delicately balanced in some cases. When strong electron-donating

Table 1—Diamagnetic susceptibilities of disubstituted benzenes

Triad No.	Compound	χ	χ_M Obs.	χ_M Calc.	$\Delta\chi_M$
		Type (i)			
1	Catechol	0.603 ± 0.002	66.3	65.5	+0.8
	Resorcinol	0.571 ± 0.002	62.8	65.5	−2.7
	Hydroquinone	0.546 ± 0.003	60.1	65.5	−5.4
2	*o*-Dimethoxybenzene	0.635 ± 0.002	87.7	87.5	+0.2
	m-Dimethoxybenzene	0.632 ± 0.001	87.3	87.5	−0.2
	p-Dimethoxybenzene	0.628 ± 0.002	86.7	87.5	−0.8
3	*o*-Phenylenediamine	0.667 ± 0.001	72.1	70.7	+1.4
	m-Phenylenediamine	0.653 ± 0.001	70.6	70.7	−0.1
	p-Phenylenediamine	0.651 ± 0.002	70.3	70.7	−0.4
4	*o*-Xylene	0.733 ± 0.001	77.8	76.3	+1.5
	m-Xylene	0.722 ± 0.001	76.6	76.3	+0.3
	p-Xylene	0.719 ± 0.001	76.3	76.3	0
5	*o*-Cresol	0.670 ± 0.003	72.4	70.9	+1.5
	m-Cresol	0.665 ± 0.002	71.9	70.9	+1.0
	p-Cresol	0.661 ± 0.001	71.5	70.9	+0.6
6	*o*-Anisidine	0.660 ± 0.002	81.2	79.1	+2.1
	m-Anisidine	0.640 ± 0.001	78.8	79.1	−0.3
	p-Anisidine	0.636 ± 0.002	78.3	79.1	−0.8
		Type (ii)			
1	*o*-Chlorotoluene	0.653 ± 0.002	82.6	80.2	+2.4
	m-Chlorotoluene	0.635 ± 0.002	80.3	80.2	+0.1
	p-Chlorotoluene	0.621 ± 0.001	78.6	80.2	−1.6
2	*o*-Bromotoluene	0.539 ± 0.002	92.2	89.1	+3.1
	m-Bromotoluene	0.525 ± 0.001	89.8	89.1	+0.7
	p-Bromotoluene	0.518 ± 0.001	88.6	89.1	−0.5
3	*o*-Iodotoluene	0.480 ± 0.001	104.6	102.7	+1.9
	m-Iodotoluene	0.477 ± 0.001	104.0	102.7	+1.3
	p-Iodotoluene	0.472 ± 0.001	102.9	102.7	+0.2
4	*o*-Chlorophenol	0.602 ± 0.002	77.4	74.8	+2.6
	m-Chlorophenol	0.589 ± 0.002	75.7	74.8	+0.9
	p-Chlorophenol	0.585 ± 0.001	75.2	74.8	+0.4
5	*o*-Fluoroaniline	0.614 ± 0.002	68.2	66.3	+1.9
	m-Fluoroaniline	0.601 ± 0.001	66.8	66.3	+0.5
	p-Fluoroaniline	0.600 ± 0.002	66.6	66.3	+0.3
6	*o*-Chloroaniline	0.624 ± 0.002	79.6	77.4	+2.2
	m-Chloroaniline	0.610 ± 0.001	77.8	77.4	+0.4
	p-Chloroaniline	0.602 ± 0.002	76.8	77.4	−0.6
7	*o*-Bromoaniline	0.516 ± 0.002	88.7	86.3	+2.4
	m-Bromoaniline	0.502 ± 0.001	86.3	86.3	0
	p-Bromoaniline	0.495 ± 0.001	85.1	86.3	−1.2
8	*o*-Iodoaniline	0.472 ± 0.001	103.4	99.9	+3.5
	m-Iodoaniline	0.454 ± 0.001	99.4	99.9	−0.5
	p-Iodoaniline	0.444 ± 0.002	97.2	99.9	−2.7

(*contd.*)

Table 1—Diamagnetic susceptibilities of disubstituted benzenes—*Contd.*

Triad No.	Compound	χ	χ_M Obs.	χ_M Calc.	$\Delta\chi_M$
		Type (*iii*)			
1	*o*-Chlorobenzoic acid	0.550 ± 0.002	86.1	84.9	+ 1.2
	m-Chlorobenzoic acid	0.560 ± 0.002	87.7	84.9	+ 2.8
	p-Chlorobenzoic acid	0.552 ± 0.001	86.4	84.9	+ 1.5
2	Ethyl *o*-Chlorobenzoate	0.575 ± 0.001	106.1	106.5	− 0.4
	Ethyl *m*-Chlorobenzoate	0.580 ± 0.002	107.0	106.5	+ 0.5
	Ethyl *p*-Chlorobenzoate	0.579 ± 0.002	106.9	106.5	+ 0.4
3	Ethyl *o*-Iodobenzoate	0.469 ± 0.001	129.4	129.0	+ 0.4
	Ethyl *m*-Iodobenzoate	0.478 ± 0.002	131.9	129.0	+ 2.9
	Ethyl *p*-Iodobenzoate	0.474 ± 0.002	130.8	129.0	+ 1.8
4	*o*-Chlorobenzonitrile	0.573 ± 0.001	78.8	78.9	− 0.1
	m-Chlorobenzonitrile	0.585 ± 0.002	80.4	78.9	+ 1.5
	p-Chlorobenzonitrile	0.583 ± 0.001	80.2	78.9	+ 1.3
		Type (*iv*)			
1	*o*-Dichlorobenzene	0.594 ± 0.002	87.3	84.1	+ 3.2
	m-Dichlorobenzene	0.589 ± 0.002	86.6	84.1	+ 2.5
	p-Dichlorobenzene	0.574 ± 0.002	84.4	84.1	+ 0.3
2	*o*-Dibromobenzene	0.443 ± 0.002	104.5	101.9	+ 2.6
	m-Dibromobenzene	0.436 ± 0.002	102.8	101.9	+ 0.9
	p-Dibromobenzene	0.428 ± 0.001	100.9	101.9	− 1.0
3	*o*-Diiodobenzene	0.398 ± 0.002	131.3	129.1	+ 2.1
	m-Diiodobenzene	0.395 ± 0.001	130.3	129.1	+ 1.2
	p-Diiodobenzene	0.388 ± 0.002	127.9	129.1	− 1.2
4	*o*-Chlorofluorobenzene	0.570 ± 0.001	74.4	73.0	+ 1.4
	m-Chlorofluorobenzene	0.567 ± 0.001	74.0	73.0	+ 1.0
	p-Chlorofluorobenzene	0.560 ± 0.001	73.1	73.0	+ 0.1
5	*o*-Bromochlorobenzene	0.492 ± 0.002	94.2	93.0	+ 1.2
	m-Bromochlorobenzene	0.486 ± 0.002	93.0	93.0	0
	p-Bromochlorobenzene	0.477 ± 0.003	91.3	93.0	− 1.7

groups are present *para* to Cl, Br and I, the importance of dπ-acceptor resonance (− M) can also become significant[5,6].

Type (i): In this class of compounds, all the triads have the highest diamagnetic susceptibilities for the *ortho* isomers, susceptibilities decreasing in the order: *ortho* > *meta* > *para*. All the *ortho* isomers have a positive exaltation. It is not additive of the substituent effects. If so, xylenes should have a negative exaltation because toluene has a negative exaltation of − 1.1 relative to the magnetic susceptibility of benzene. In the same way *o*-phenylenediamine should have a negative exaltation because the amino group in aniline has a value of − 0.6. But it has a positive exaltation of 1.3. A single electron-releasing group, attached to the benzene ring and in conjugation with it, always tends to lower the diamagnetic susceptibility of the ring. When this conjugation is sterically inhibited by the presence of another substituent of a similar kind or type, the magnetic susceptibility of the ring seems to be restored to almost its original value. This may be the reason for the positive $\Delta\chi_M$ values observed for *ortho*-substituted benzenes where both the substituents are electron-releasing. The *para*-isomer has the lowest value. This may be due to the mutual opposition to electron-release by the substituents and thus the benzene ring has the least electron gain. There are undoubtedly other factors such as polar, field and steric effects. Diamagnetic susceptibility is affected by intermolecular and intramolecular H-bonding. The H-bonding decreases magnetic susceptibility[7,8]. This fact must be taken into account while understanding the magnetic susceptibilities of phenols (triad 1).

Type (ii): These compounds also show a behaviour similar to that of type (i) compounds. The electron-withdrawing mesomeric effect (− M) of Cl, Br and I becomes apparent only when the *para* substituent is a powerful electron-releasing group like NH_2. Then there is conjugation of the *para* substituents through the benzene nucleus leading to a fall in diamagnetic susceptibility. This is observed only in the case of chloro, bromo and iodo compounds but

Table 2—Diamagnetic susceptibilities of trisubstituted benzenes

Compound	χ	χ_M Obs.	χ_M Calc.	$\Delta\chi_M$
Dimethylphenols				
2,3-Dimethyl	0.688 ± 0.001	84.0	81.6	+2.4
2,6-Dimethyl	0.684 ± 0.002	83.5	81.6	+1.9
2,4-Dimethyl	0.684 ± 0.001	83.5	81.6	+1.9
2,5-Dimethyl	0.681 ± 0.001	83.1	81.6	+1.5
3,4-Dimethyl	0.685 ± 0.002	83.6	81.6	+2.0
3,5-Dimethyl	0.678 ± 0.001	82.8	81.6	+1.2
Dimethylanisoles				
2,3-Dimethyl	0.698 ± 0.001	95.0	92.6	+2.4
2,6-Dimethyl	0.693 ± 0.001	94.3	92.6	+1.7
2,4-Dimethyl	0.693 ± 0.002	94.3	92.6	+1.7
2,5-Dimethyl	0.690 ± 0.001	93.9	92.6	+1.3
3,4-Dimethyl	0.695 ± 0.002	94.5	92.6	+1.9
3,5-Dimethyl	0.689 ± 0.001	93.8	92.6	+1.2
Trihalogenobenzenes				
1,2,3-Trichloro	0.574 ± 0.002	104.1	98.7	+5.4
1,2,4-Trichloro	0.555 ± 0.001	100.7	98.7	+2.0
1,3,5-Trichloro	0.512 ± 0.001	92.9	98.7	−5.8
1,2,3-Tribromo	0.416 ± 0.002	130.9	125.4	+5.5
1,2,4-Tribromo	0.392 ± 0.001	123.4	125.4	−2.0
1,3,5-Tribromo	0.372 ± 0.002	117.0	125.4	−8.4

not in the case of *p*-fluoroaniline. The Cl, Br and I, having vacant *d*-orbitals in their valence shells, can take the electron released by the *p*-amino group[6] but not F.

Type (iii): In this group the *meta*-isomer has the highest value, the magnetic susceptibilities decreasing in the order, *meta* > *para* > *ortho*. The COOH and COOEt groups, being electron-withdrawing, behave like the nitro group. Why nitrobenzene has a higher diamagnetic susceptibility than benzene, in spite of the nitro group's conjugation with the benzene ring, was explained in an earlier paper[4]. But it is not clear why the *meta*-isomers have significantly high $\Delta\chi_M$ values, although the *para*-isomers have lower values. In this context it may be noted that among chloronitrobenzenes the *para*-isomer has the lowest value[4] due to strong conjugative interaction of the Cl- and -NO_2 substituents. It is interesting to note that *p*-chlorobenzonitrile, which has also an electron-withdrawing group *para* to the Cl substituent, has a $\Delta\chi_M$ of +1.4, thus indicating no significant conjugative interaction of the *para* substituents. The obvious conclusion is that the −CN is a weaker electron-withdrawing group than −NO_2 and that it is not strong enough to make the −Cl an electron-donor (for this, its +M effect should outweight its −I effect). The COOEt is also comparable to CN in this respect. The *ortho*-isomers of type (iii) triads have the lowest $\Delta\chi_M$ values presumably due to the steric effects that usually go with them.

Type (iv): All the triads show the highest diamagnetic susceptibilities for the *ortho*-isomers, the susceptibilities decreasing in the order: *ortho* > *meta* > *para*. The high $\Delta\chi_M$ values of the *ortho*-isomers cannot easily be explained, although the reason can be due to crowding of the substituents, as the same effect is seen even to a much greater extent in 1,2,3-trihalogenobenzenes. As the halogeno substituents come closer in *ortho* positions, the non-bonded electrons of the atoms repel each other and affect the motions of the nuclei and electrons, which in turn cause changes in magnetic susceptibility. The significantly high $\Delta\chi_M$ values observed for *m*-dihalogenobenzenes also reveal the possible interactions between the positive charges that the halogeno substituents set up on the benzene carbons and the nonbonded electrons of the attached halogeno substituent. These effects are more prominently observed in trihalogenobenzenes as well, as seen later The observed magnetic susceptibilities of *p*-

Table 3—Applicability of principle of additivity

Trisubstituted benzene	$\Delta\chi_M$	Exaltations in disubstituted benzenes*				$\Delta\chi_M$ (1)+(2)
			$\Delta\chi_M$ (1)		$\Delta\chi_M$ (2)	
2,3-Dimethylanisole	2.4	*o*-Xylene	1.5	*m*-Methylanisole	0.8	2.3
2,4-Dimethylanisole	1.7	*o*-Methylanisole	1.3	*p*-Methylanisole	0.6	1.9
2,5-Dimethylanisole	1.3	*o*-Methylanisole	1.3	*p*-Xylene	0	1.3
2,6-Dimethylanisole	1.7	*o*-Methylanisole	1.3	*m*-Xylene	0.3	1.6
3,4-Dimethylanisole	1.9	*o*-Xylene	1.5	*p*-Methylanisole	0.6	2.1
3,5-Dimethylanisole	1.2	*m*-Methylanisole	0.8	*o*-Xylene	0.3	1.1
2,3-Dimethylphenol	2.4	*o*-Xylene	1.5	*m*-Cresol	1.0	2.5
2,4-Dimethylphenol	1.9	*o*-Cresol	1.5	*p*-Cresol	0.6	2.1
2,5-Dimethylphenol	1.5	*o*-Cresol	1.5	*p*-Xylene	0	1.5
2,6-Dimethylphenol	1.9	*o*-Cresol	1.5	*m*-Xylene	0.3	1.8
3,4-Dimethylphenol	2.0	*o*-Xylene	1.5	*p*-Cresol	0.6	2.1
3,5-Dimethylphenol	1.2	*m*-Xylene	0.3	*m*-Cresol	1.0	1.3

*Values for *o*-, *m*- and *p*-methylanisoles are from Baliah and Abubucker[4].

chlorofluorobenzene, *p*-dichlorobenzene and *p*-chloroiodobenzene agree reasonably well with the calculated values. But the other *p*-dihalogenobenzenes have significantly high negative $\Delta\chi_M$ values. The reason for this is not clear.

Trisubstituted benzenes

The diamagnetic susceptibility is the highest for 2,3-dimethylphenol in which the crowding of substituents is the highest. Then come 2,6-dimethylphenol and 3,4-dimethylphenol. The lowest value is for 3,5-dimethylphenol in which the substituents are staggered and least crowded.

The same trend is observed in the case of dimethylanisoles. Trichlorobenzenes and tribromobenzenes also exhibit a similar behaviour. The differences in the diamagnetic susceptibilities of trihalogenobenzenes are very striking and strongly suggest that the crowding of substituents contributes significantly to the diamagnetic susceptibility. It is interesting that 1,3,5-trichlorbenzene and 1,3,5-tribromobenzene have diamagnetic susceptibilities which are appreciably lower than the calculated values. The reason for their large negative $\Delta\chi_M$ values is not clear.

Another interesting observation made concerns the principle of additivity. The $\Delta\chi_M$ of any of the dimethylanisoles or dimethylphenols is approximately the sum of the $\Delta\chi_M$'s of two disubstituted benzenes (the substituents of these compounds being any two of the three found in the trisubstituted benzenes). The two disubstituted benzenes are to be chosen in such a way that the positions of the substituents relative to those found in the trisubstituted benzene remain the same but in one the substituents occupy the closest possible positions and in the other the substituents occupy the farthest possible positions. This is exemplified by 3,4-dimethylanisole: The sum of the $\Delta\chi_M$ of *o*-xylene (1.3) and that of *p*-methylanisole (0.6) is 1.9 which is almost the same as the $\Delta\chi_M$ of 3,4-dimethylanisole. For other compounds the additivity principle is shown in Table 3.

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