

DIAMAGNETISM AND CHEMICAL BONDING

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INTRODUCTION

SINCE Michael Faraday⁴ classified substances into the now well-known magnetic groups, a considerable amount of work, not all systematic nor of the same degree of accuracy, has been done and the names of Curie, Pascal and Langevin are associated with the earlier fundamental work on diamagnetism. The most extensive and reliable experimental work especially with organic compounds has been carried out by Pascal during a period of over fifteen years⁹ and by a careful analysis of his results, deduced the relationship

$$\chi_M = \Sigma \chi_A + \lambda, \quad (1)$$

where χ_A represents the susceptibility of each of the constituent atoms in combination and λ a small constitutive correction term which varies with each homologous series. This correlation between susceptibility and chemical constitution no doubt served a useful purpose at the time but the theoretical justification or physical meaning of these correction terms has not been made clear. In fact the very success of the correspondence between "calculated" and observed values of susceptibility has been a deterrent against any other approach and even recent publications on the subject^{1,2,11,16} generally pass over the subject with the remark that diamagnetic susceptibility has no diagnostic value in structure determinations.

The original Langevin expression for diamagnetic susceptibility assuming no paramagnetism, in the form given by Pauli¹⁰ gives for the molar susceptibility

$$\chi = - \frac{Ne^2}{6mc^2} \Sigma \bar{r}_i^2 \quad (2)$$

This expression has been derived on the assumption that the molecule has no electronic angular momentum in the absence of a field. The advent of the new quantum theory has naturally resulted in a modification of the classical relationship.² For a polyatomic molecule with a spin quantum number zero, which is the most common value for all even molecules, the molar susceptibility is given by equation (3) (ref. 18)

$$\chi_M = - \frac{Ne^2}{6mc^2} \Sigma \bar{r}^2 + \frac{2}{3} N \Sigma_{n' \neq n} \frac{|m(n', n)|^2}{h\nu(n', n)} \quad (3)$$

A compound is diamagnetic or paramagnetic according as the first or the second part of the expression on the right-hand side of equation (3) makes a larger contribution. The various theoretical evaluations that have been derived^{1,11,16,18} differ essentially only in their mode of obtaining the value of Σr^2 . In his derivation of screening constants required for the purpose, Slater makes no distinctions between the *s* and *p* orbitals but the conception of *sp* hybridisation has been so successful in interpreting the behaviour of carbon compounds that one may reasonably assume the accuracy of evaluation by Slater's method in the case of compounds of carbon with other elements especially of the first short period. The second part of the expression, however, has to be computed empirically in the case of polyatomic molecules making the justifiable assumption that the formation of a covalent bond can be associated with a contribution to the paramagnetic term. This constitutes essentially the bond depressions reducing the computed value of diamagnetic susceptibility.

THE EVALUATION OF BOND DEPRESSIONS

When Pascal attempted to correlate diamagnetic susceptibility with chemical constitution, the nature of valency was imperfectly understood. The correction terms introduced by him were obvious necessities, as they were with all other correlations between physical properties and chemical structure. A different interpretation is, however, called for with the advent of the electronic and quantum theories of valency. The first attempt in this direction were made by Gray and co-workers,⁷ who used Pauling's method of evaluating Σr^2 . They evaluated the contribution to molar susceptibility by each atom by making use of Sidgwick's method¹³ for charge distribution in a polar link. In arriving at bond depression values, use was made of the observed susceptibility of diamond and of the methylene group. These gave the bond depression values for a carbon-carbon single bond and a carbon-hydrogen bond. With these as the starting points, and taking a select number of suitable number of standard substances, values for bond depressions of other bonds were obtained. In their interpretation of resonance hybrid structures, even with benzene and naphthalene, ionic structures with alternate carbon atoms carrying a positive and a negative charge have been postulated, and the remarkable agreement obtained between 'calculated' and experimental values can only be a fortuitous coincidence. Further, the distinction that is drawn very often between covalency and co-ordinate covalency is arbitrary and has no physical meaning.^{11a}

In the present communication, bond depression values have been computed by following Gray's method, with the modification that ionic susceptibility values have been calculated by Slater's method¹⁵ and the modification

by Angus.¹ Also no distinction between the two 'types' of covalency have been made and the diamagnetic susceptibility of diamond recently reported by A. Sigamony¹⁴ has been used in preference to the higher value previously used as this was found to give greater concordance between calculated and observed values in the case of all the compounds listed below.

The bond depressions thus obtained are given in Tables I, II and III. (All susceptibility values are in units of 10^{-6} .)

TABLE I. *Bond Depressions of Carbon-Carbon and Hydrogen-Carbon Linkages*

Bond	P	S	A	Compound used as standard
C - C	1.98	2.08	1.34	Diamond
C = C	9.50	7.68	6.63	Δ : 1 Octene
$C_{ar} - C_{ar}$	2.84	2.38	1.49	Benzene
$C \equiv C$	6.73	3.43	4.63	Heptene-1
H - C	1.06	0.25	-0.43	Methylene group

TABLE II. *Bond Depressions of other bonds, single and multiple*

Bond	S	A	Standard
C - O	2.39	2.89	Diethyl ether
C = O	10.53	10.42	Acetone
C - N	1.64	3.20	Tri-isobutyl amine
C = N	12.30		Isobutyraldoxime
$C \equiv N$	4.40		<i>n</i> -butyronitrile
C - Cl	3.85		<i>n</i> -propyl chloride
N - O	1.90		Ethyl hydroxylamine
N = O	10.24		Nitroso benzene
H - N	0.45	-1.08	Diethyl amine
H - O	2.16	1.07	Methyl alcohol

TABLE III. *Bond Depressions of other links involving resonance*

Bond	Depression	Standard
C - Cl	5.57	Chlorobenzene
C - N	3.80	Aniline
N ... O	6.30	Nitro group

It will be observed from the tables that whatever be the method of calculation adopted,* the bond depressions of a single bond between two

* In the first four tables in this paper, the letters P, S, and A at the head of a column indicate that the ionic susceptibility values used in the calculations have been obtained by the Pauling, Slater or Angus methods.

atoms are as a rule very much less than that of a double bond between the same two atoms, while a triple bond between them affects the susceptibility to a much smaller degree than the double bond. Also it will be noticed from Table III that some of the bond depressions lie between those of a single and a double bond.

Using these bond depression values, the diamagnetic susceptibility† of a number of compounds have been calculated and the results are given in Table IV. These clearly indicate that the agreement between calculated

TABLE IV

Compound	Calculated Values			Observed Values (8)
	P	S	A	
<i>n</i> -Hexane C ₆ H ₁₄	75.5	76.0	75.5	76.4
<i>n</i> -Octane C ₈ H ₁₈	98.8	99.2	103.9	99.5
Cyclohexane C ₆ H ₁₂	70.0	69.7	72.9	68.2
Trimethyl Ethylene	52.8	54.6	56.8	54.1
Cyclohexene	58.0	60.0	61.8	58.4
Toluene	68.4	67.1	67.6	67.1
<i>m</i> -Xylene	80.0	78.8	79.7	78.8
<i>p</i> -Cymene	103.4	102.0	104.0	103.1
Diphenyl Methane	119.6	116.4	116.3	115.2
Triphenyl Methane	170.8	165.7	165.0	164.6
Acetal CH ₂ C (OEt) ₂		85.1		85.8
Cineol-1 : 4		116.3		116.1
Ethyl Alcohol	34.4	32.9	33.4	33.5
<i>n</i> -Propyl Alcohol	47.1	44.5	45.4	46.0
Benzyl Alcohol	72.0	70.5	69.7	73.3
Ethylene Glycol	39.6	36.2	34.0	38.7
Acetaldehyde	21.9	22.8	22.2	22.1
Propionaldehyde	33.2	34.0	34.0	34.0
<i>n</i> -Butyraldehyde	44.9	45.6	46.1	45.8
Benzaldehyde	57.4	58.8	57.4	60.8
Methyl Ethyl Ketone	44.9	45.6	46.1	45.6
Methyl-Propyl Ketone	56.5	57.2	58.3	57.5
Methyl <i>n</i> -butyl Ketone	68.2	68.9	69.5	69.1
Methyl <i>n</i> -Hexyl Ketone	91.6	92.2	93.7	93.3
Acetophenone	71.3	70.9	69.9	72.4
Benzophenone	108.7	107.1	106.1	108.2
Camphor		103.4		103.4
Tri-isoamyl amine		190.5	192.3	192.1
Ethylamine		63.3	58.5	61.0
<i>o</i> -Toluidine		74.3	74.6	74.4
Phenyl Hydroxylamine		69.8		68.8
Benzonitrile		63.9		67.1
Nitrobenzene		61.1		61.5
Methyl chloride		31.9		32.0
Methylene chloride		46.4		46.7
Chloroform		59.6		58.4
Carbon tetrachloride		74.7		67.4
Tetra chlorethylene		84.3		84.2

† Since only diamagnetic substances have been considered the negative sign that should precede the susceptibility values have been omitted for convenience. A negative sign in the bond depression means an increase in diamagnetic susceptibility.

and observed values is consistently better with the Slater and Angus values of ionic diamagnetic susceptibility than those with the Pauling values and of the two, the Slater values give a slightly better agreement. Further, the apparent increase in diamagnetic susceptibility (negative value for bond depression) by using the Angus values for the formation of a C—H link or an O—H one while the N—H link behaves differently is not in keeping with the usual periodic gradation and as such the Slater method has been preferred.

BOND DEPRESSIONS AND BOND ORDER

Accurate determinations of bond distances by spectroscopic, X-ray and electron diffraction methods have shown that a number of compounds reveal bond distances intermediate between those of a single and a double bond. This behaviour has been invariably met with in the case of compounds whose normal behaviour requires the postulate of resonance hybrid structures. An empirical curve can be drawn^{7, 11a} showing the relationship between bond distance and bond order.

Other properties that can be associated with these bonds also have been found to show a similar relationship.⁶ It is, therefore, not unreasonable to consider that bond depressions can also be similarly correlated and the curve obtained (Fig. 1).

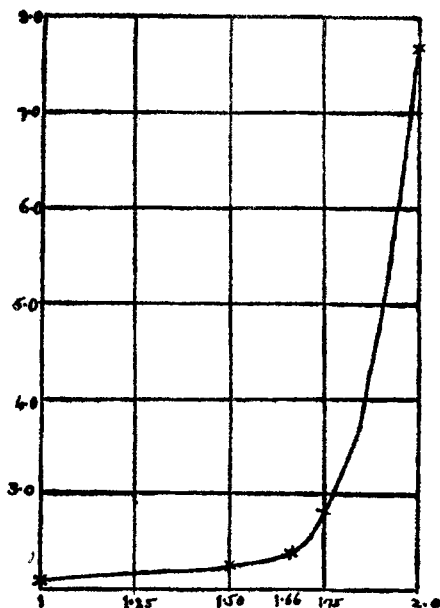
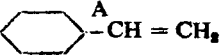
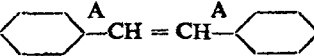


FIG. 1

It is found on examination that while the change from a single bond to a double bond leads to a progressive increase in the value of the bond

depression, with the largest increase between bond order 1.66 and 2, the change to a triple bond records a distinct fall. Any explanation for this must necessarily be traced to the nature of the electrons in a triple link. The accuracy of the correlation possible is clearly demonstrated by the agreement between calculated and observed values in the case of a few compounds (listed in Table V) in which bond orders are known from other data.

TABLE V. *Bond Order and Diamagnetic Susceptibility*

Substance	Bond order of A (Pauling)	Calculated Susceptibility	Observed Susceptibility
Styrene 	1.5	68.7	68.2
Stilbene 	1.5	118.3	119.9
Heptene-2 $\text{H}_2\text{C} \overset{\text{A}}{\text{C}} \equiv \overset{\text{A}}{\text{C}} - \text{CH}_2 \cdot \text{C}_2\text{H}_5$	1.2	77.2	75.7
Cyanogen $\text{N} \equiv \overset{\text{A}}{\text{C}} - \text{C} \equiv \text{N}$	1.45	22.0	21.6

The halogens are usually considered to be monovalent in combination with carbon, but the measurement of dipole moment as well as the measurement of bond distances by the various methods available for the purpose indicate that, in some of the compounds at least, the carbon-halogen bond has double-bond character. The bond depression values in Table VI clearly show that the same conclusion can be drawn from diamagnetic susceptibility measurements also. If one might generalise from the figures, it appears that the carbon-halogen bond in chloroacetone should have about 15% double bond character. It is interesting to note in this connection that tetrachlorethylene listed in Table IV appears to behave normally. The explanation for this apparent behaviour is traceable to a mutual compensation that is possible in this halogenoethylene. The carbon-carbon double bond is known to be stretched towards the side of single-bond character and the consequent reduction in the bond depression value offsets the increased bond depression of the carbon-chlorine bond which has about 5% double bond character.

TABLE VI. *Double Bond Character of Carbon-Chlorine Bonds*

Compound	% Double bond character	Carbon-chlorine bond depression
Chlorobenzene	15	5.50
Vinyl Chloride	18	5.45
Dichlorethylene	18	5.50
Chloracetone	?	5.50

With the uncertainty regarding the purity and experimental accuracy of the other halogen compounds, that have been measured no general correlation is feasible at present. The large discrepancy in the calculated and observed value for carbon tetrachloride also needs an explanation. Double bonded character cannot be completely excluded judging from the small but definite shortening in the carbon chlorine distance in this compound, but this by itself may not account for the whole discrepancy.

Diamagnetic Susceptibility of Ions

The greatest degree of variation between calculated and observed susceptibilities are met with in the case of ions whether in the solid state or in solution. The difficulty naturally has been because it is not possible to determine experimentally the susceptibility of only one species of ions without the interference of other ions. Methods of approximation used to eliminate the interfering factor partly account for the differences among the workers. The use of measurements on the pure acids by Reichenander and other later workers^{5,12} suffers from one important defect. While the assumption that the proton makes no contribution to susceptibility is correct, one must recognise that no free proton exists in the solution of any acid. It is invariably present in water as a solvated ion as OH_3^+ . The formation of this new entity must necessarily alter the susceptibility of the solvent and to this extent, the evaluations are in error.

In the course of the evaluation of bond depressions, the necessary data for evaluating the ionic diamagnetic susceptibilities of the ammonium ion and the nitrate ion have been obtained, and the susceptibility of the salt ammonium nitrate could be naturally evaluated. It can be seen from the following table (Table VII) that the value thus obtained agrees quite satisfactorily with the value reported by Trew¹⁷ for this compound.

TABLE VII. *Susceptibility of Ammonium Nitrate*

$\chi_{\text{NH}_4^+}$: 13.8	$\chi_{\text{NO}_3^-}$: 18.5
$\chi_{\text{M}} \text{NH}_4\text{NO}_3$: 32.3	
$\chi_{\text{M}} \text{observed}$: 32.6	

Using these values as standards for ionic susceptibilities, one may then build up from known values of molar susceptibilities of salts, the susceptibilities of other ions. The values thus obtained for the alkali and halide ions are appended in Table VIII.

TABLE VIII

Susceptibilities of the alkali metal and the halide ions

Lithium	0.9	Fluoride	9.2
Sodium	6.7	Chloride	22.9
Potassium	15.9	Bromide	33.4
Rubidium	23.0	Iodide	50.2
Cæsium	35.5		

These values again differ from those calculated by Slater. Presumably, the approximations used while satisfactory in the case of short period elements excepting the very lightest, are not so accurate for the long periods.

CONCLUSION

From the foregoing pages, it will be noticed that an interpretation of diamagnetic susceptibility data is possible by the use of bond depression values and ionic susceptibilities taking into account our knowledge of the nature of bonds involved. While the limitations of experimental accuracy exist, these measurements are useful as a check, where other methods indicate definite possible structures for an organic compound. The values obtained by this method for the ammonium and nitrate ions also provide a means of checking the ionic susceptibility of other ions.

SUMMARY

Using the method of Gray but with the values of ionic susceptibilities derived by Slater's method, bond depression values have been set up for various linkages. With these values, the molar susceptibility of a large number of compounds have been calculated and a close agreement between the calculated and observed values is obtained. An empirical correlation is found between bond-order and bond-depression and the results clearly indicate the double bonded character of certain carbon-carbon and carbon-halogen linkages. A method of evaluating ionic susceptibilities using ammonium and nitrate ions as standards is indicated.

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