

THE HYDROGEN BOND AND DIAMAGNETISM

BY S. V. ANANTAKRISHNAN AND P. S. VARADACHARI

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1. Introduction

THE interpretation of susceptibility data in terms of atomic contributions with a few "constitutive corrections" developed by Pascal¹⁹ has been so successful that even recent studies make no attempt to depart from this rule. Pauling²¹ is constrained to remark "Diamagnetic polarisation can be calculated with reasonable accuracy as the sum of terms corresponding to the atoms composing the substance with, perhaps, some small corrections for the type of bonds involved. Diamagnetic polarisation has not been found to be of much value in the investigation of the structure of molecules." However, attempts have been made by Gray and co-workers^{10, 14} to interpret diamagnetic data in terms structure and though 'calculated' and 'observed' values show remarkable agreement, the coincidence as will be shown in a later communication, is largely fortuitous.

Among structures that influence physical properties of organic compounds, hydrogen bonds have been known to cause noticeable deviations from usual laws while the methylene group has been found to exert a remarkably constant influence on these properties when one compares the members of different homologous series.^{26, 20} One may reasonably expect, therefore, that, taking these two factors, the extent to which hydrogen bonding alters diamagnetic susceptibility may be gauged. Other investigations^{5, 22} show that hydrogen bonding may be intramolecular or intermolecular while a weaker type has been designated by Bernal and Fowler⁶ the 'hydroxyl bond'.

Apart from a preliminary report by Angus and Hill¹ there does not appear to be any special study of the problem and the present survey is a prelude to a systematic structural interpretation of diamagnetism. In the comparison of susceptibility values, the question of choice between the results of different workers arises. For a proper comparative study, a necessary and sufficient condition is that values should be self-consistent and any deviation to be interpreted must be beyond the limits of experimental error. These limitations preclude any correct interpretation in some cases even if other physical properties indicate the existence of a

hydrogen bond. The results of Angus and Hill (*loc. cit.*), the only magnetic investigation of the hydrogen bond, illustrate this point as may be noticed from their data presented in Table I for benzoic and salicylic acids.

TABLE I

Substance	Solvent	<i>c</i> (wt. %)	Solution	Solute	Solvent	
Benzoic Acid	Benzene	2.73	0.702 ₅	0.720	0.702	0.004
		4.05	0.7020	0.685?		
6.13		0.698 ₈	0.650			
	Ethyl acetate	3.33	0.606 ₈	0.432	0.612 ₅	0.003
		5.81	0.6050	0.483		
Salicylic Acid	Chloroform	1.28	0.516 ₅	0.632	0.515	0.002
		1.49	0.5160	0.582		
	Ethyl acetate	4.89	0.6120	0.602		
		6.91	0.6077	0.543		

It will be noticed that all the susceptibility values are for very dilute solutions and lie within the limits of possible experimental error. From a later section it will be found that the change in diamagnetism of a polyatomic molecule through hydrogen bonding cannot be as large as one might infer from the χ_{solute} values and the variations with even changes of concentration appear to be abnormally large. It may be mentioned, however, that the changes observed in the case of solutions of benzoic acid are in the right direction. Judging from these results, one has to conclude that the study of dilute solutions may not be a fruitful line of approach to the problem of hydrogen bonding. A different approach is therefore indicated.

2. Intramolecular Hydrogen Bonds

Well-known examples of intramolecular hydrogen bonding are found in aromatic compounds. Taking closely related structures differing only by the presence of a hydroxyl group, molar susceptibility values may be expected to indicate hydrogen bonding. Though phenol is considered to be associated, the work of Badger and co-workers^{4, 5} indicates that no serious error will be introduced by taking it as unassociated for our present purpose. The susceptibility data for a few closely related structures are given in Table II.

The first two pairs of compounds indicate that the replacement of a hydrogen by hydroxyl in a six-membered ring brings about the same change in susceptibility. Substances A in the latter pair are known to involve hydrogen bonded structures and the extra contribution to diamagnetic susceptibility may naturally be traced to this factor. The net increase in the value works

TABLE II
(Values taken from *I.C.T.*)

Substance A	Substance B	x_A	x_B	x_{M_A}	x_{M_B}	$x_{M_A} - x_{M_B}$
Cyclohexanol	Cyclohexane	0.726	0.810	72.6	67.3	5.3
Phenol	Benzene	0.648	0.712	60.9	55.4	5.5
Methyl salicylate	Methyl benzoate	0.580	0.602	88.2	81.9	6.3
2 : 4-Dinitro phenol	<i>m</i> -Dinitro benzene	0.397	0.398	73.0	67.0	6.0

out to nearly one unit per mole and incidentally indicates this as an alternative method that can be advantageously used in the study of hydrogen bonding especially in compounds of low molecular weights.

3. Intermolecular Hydrogen Bonds

If, as has been noticed in the previous section, hydrogen bonding increases the diamagnetism, the reverse process of rupture of hydrogen bonds should lead to a decrease. The conversion of an aliphatic carboxylic acid to the corresponding methyl ester involves not only the addition of a methylene group but also the rupture of the hydrogen bonds in the dimer found normally in all liquid and solid aliphatic acids at room temperature.¹³ Consequently, the apparent contribution to the molar susceptibility by the methylene group should appear to be smaller than the normal value by about one unit as the change involves the rupture of one hydrogen bond per molecule.

Ignoring the very low value reported by Bhatnagar and co-workers⁷ it is generally found that the increase in χ_M caused by the addition of a $-\text{CH}_2$ group is 11.69×10^{-6} per mole and one may justifiably assume the constancy of this value for calculations. The agreement among the different workers may be seen by examining the data in Table III and the curves in Fig. 1.

TABLE III

Acid	x_{Angus} (2)	x_{P} (12)	$x_{\text{I.C.T.}}$ (16)	$x_{\text{B.N.}}$ (23)	x used	x_M
Formic	0.432	0.433	0.433	19.88
Acetic	0.528 ₃	..	0.526	0.525	0.528	31.72
Propionic	0.585 ₃	..	0.587	..	0.585	43.36
Butyric	0.626 ₅	0.625 ₃	0.632	..	0.627	55.20
Valeric	0.654 ₈	0.655	66.85
Caproic	0.676 ₂	0.673 ₀	0.676	78.14
Heptylic	0.6900	0.690	89.74
Caprylic	0.7053	0.705	101.6

Plotting χ_M against the number of methylene groups n (CH_2) it will be noticed from Fig. 1 that all the points lie on a straight line and by extrapola-

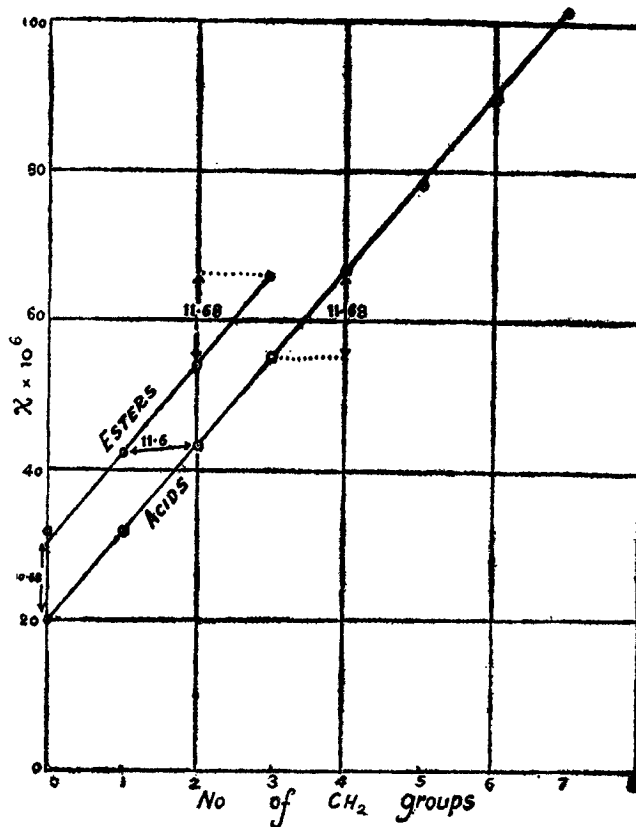


FIG. 1

tion from the curve, the diamagnetic contribution per methylene group works out to 11.69. Substitution of hydrogen by CH₂ in the alkyl part of the carboxylic acid does not, therefore, imply any abnormality. It will be noticed from Table IV and Fig. 1 (a) that the replacement of carboxyl hydrogen is different.

TABLE IV

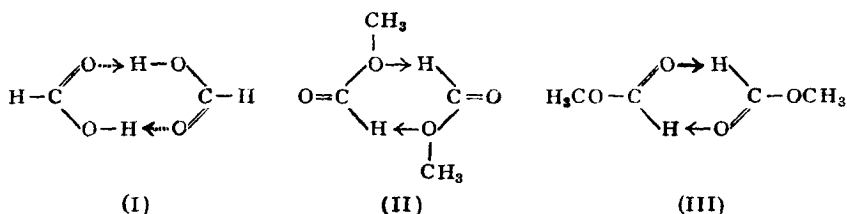
Acid	χ_M acid*	χ_M ester calculated	χ ester	χ_M ester observed†	Difference between calculated and observed χ_M values of esters
Formic	19.86	31.52	(0.5267)	31.60	-0.08
Acetic	31.72	43.36	0.5719	42.34	0.98
Propionic	43.35	55.04	0.6136	54.04	1.01
Butyric	55.20	66.84	0.6446	65.79	1.05

* χ_M is calculated assuming the monomeric form of the acid alone.

† The value for formic ester is that given by Rao and Narayanaswami.⁴³ Higher values reported can be traced to water present as impurity which is difficult to remove in this case.

Angus (*loc. cit.*) has observed that in changing from the acid to the methyl ester, the diamagnetic contribution of the methylene group is 10.69 or one unit less than the normal value.

Assuming the constancy of the methylene group contribution, it will be noticed from the last column that the difference between the calculated and observed values of the esters is just one unit per mole, a difference that may be expected for a dimer with one hydrogen bond per molecule (*vide* Section 6). The first member behaves abnormally. Like all other carboxylic acids, the dimeric form of formic acid has structure I, the C-H hydrogen being free.* If the acid is converted into the methyl ester, the hydrogen bonds of the carboxyl group is destroyed but a new set of dimers having the alternative structures II or III involving the C-H hydrogen is presumably formed.†



Since the number and nature of the hydrogen bonds apparently remain the same in both the acid and the ester, the contribution by the methylene group appears normal. Methyl formate is thus abnormal when compared with the other methyl esters and the point corresponding to methyl formate on the $\chi_M-n\text{CH}_2$ curve (Fig. 1 a) does not fall in line with the rest as it happens to be dimeric involving a hydrogen bond.

In a later section it will be shown that the provable structure is II and not III since it involves $\text{C}=\text{O}$ as in the acids and as such may be expected to have the same effect on susceptibility. The Raman spectrum with a modified C-H frequency^{18, 24} confirms this view and the carbonyl frequency also supports the same idea.

Mention should also be made here of Angus's observation² that the change in susceptibility noticed between formic acid and the formate ion is due to hydrogen bonding in the acid. From our foregoing analysis it will be noticed that the change caused by hydrogen bonding in the molar

* The Raman spectrum of formic acid²⁰ shows a normal C-H frequency which will not be the case if it were involved in hydrogen bonding as in the complex of the type postulated by Murti and Seshadri.¹⁸ The feeble second carbonyl frequency is traceable to the known existence of about 10% monomer even at room temperature.¹³

† Methyl formate has higher m.p. than methyl acetate indicating complexity.

susceptibility is small though definite. The large observed difference between the acid and the ion has probably arisen more from the structural changes in the carboxyl group. The non-equivalence of the resonance structures and presumably different carbon oxygen bond-lengths in the case of formic acid and the equivalence in the formate ion may give rise to the observed difference. This view is supported by the Raman spectrum which indicates no carbonyl frequency in the case of formates.²⁹

4. *Alcohols and Water*

Unlike the cases considered in the previous sections, the alcohols and water (which may be considered the first member in the homologous series R-OH) show variations of a different type. It is recognised that all abnormal physical properties of this class of compounds result from association through hydrogen bonding.²² In order to differentiate these weak polarisation bonds, Bernal and Fowler⁶ have in their theory of a quasi-crystalline structure of liquid water postulated a hydroxyl bond. The work of Cabrera and Fahlenbrach⁹ on water and a series of alcohols as well as that of Auer on water³ seem to indicate a small but definite increase in diamagnetic susceptibility with temperature (*cf.* also Varadachari²⁸). Since rise of temperature can reasonably be expected to favour depolymerisation, this implies that the monomer has a higher diamagnetic susceptibility than the dimer, a result apparently the opposite of what has been noticed in the case of carboxyl compounds. This will be discussed in a later section.

5. *Inorganic Oxy Acids*

If one assumes as in the organic acids that the methylene group contribution to diamagnetic susceptibility is a constant, the observed susceptibility of dimethyl sulphate ($\chi_M 62.12$)¹⁶ leads to a χ_M value for sulphuric acid of 38.84. The careful investigations of Farquharson¹¹ gives an experimental value of 42.3 for pure sulphuric acid confirming the value given in *International Critical Tables*. This large difference may be attributed to hydrogen bonding and other physical properties also indicate the possibility of larger aggregates in 100% sulphuric acid.

The case of iodic acid is even more interesting. The χ_M value changes from 47.01 in the crystalline orthorhombic form to 41.47 in solution. This large difference in the susceptibility is partly due to the break up of the hydrogen bonds present in the crystal and partly to ionisation in solution. The investigations of Helmholtz and Rogers¹⁵ have shown that the crystal with a unit cell of four iodic acid molecules contains bifurcated hydrogen bonds.

A proper discussion of the contribution of hydrogen bonds to the diamagnetism of inorganic acids is, however, not feasible at present especially since most of the data are derived from the measurements with corresponding salts and as such unsuitable for interpretations of this nature.

6. *The Nature of the Hydrogen Bond and its Contribution to Diamagnetism*

Since diamagnetism is liable to be influenced by the interaction of orbital electrons, the change in diamagnetism in hydrogen bonded structures should be related to the nature of such bonding. Earlier views implied an apparent increase in the covalency of hydrogen but this has been severely criticised. The hydrogen bond may now be treated as an essentially hybrid structure, the resonance involving hydrogen attached to one atom by a true covalency and the other by an electrovalency.

In any structure



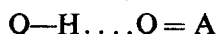
the distance between the atoms A, B taking part in the hydrogen bond is invariably found to be less than in the case for an isolated pair of atoms and the shorter this distance the greater the strength of the hydrogen bond. The structure may be more correctly pictured as essentially arising from the location of a proton at an equilibrium distance with the bonding electrons more spread out between the two extreme positions.

Following Van Vleck²⁷ the diamagnetism of a polyatomic molecule may considered to involve a paramagnetic term arising from the distortion of the orbital electrons and a diamagnetic term. Both these are independent of temperature. The formation of a hydrogen bond can influence the diamagnetic susceptibility in four directions:—

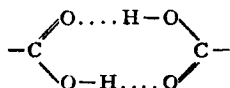
1. Increased diamagnetism through the spreading of the electron cloud or the formation of larger molecular orbitals of the bonding electron.
2. Decrease in the paramagnetism associated with the bonds through a release of strain in the groups involved. This is likely to be appreciable only in the cases where multiple linkages are involved.
3. The formation of an additional bond make a small paramagnetic contribution through the distortion of the electron orbits.
4. A large diminution in diamagnetism resulting from a distortion of the orbits and a decrease in the effective area through the presence of a proton inside the electron cloud of two atoms connected by hydrogen bonding.

Any change noticed that has to be a resultant of all these factors.

An analysis of the structures involved in hydrogen bonding shows that we can broadly divide them into two categories according as multiple bonds or single bonds are involved. Examples of the first type are provided by carboxylic acids, esters of salicylic acid, nitrophenols and sulphuric acid, all of which involve structures of the type



where A stands for carbon, nitrogen or sulphur. As mentioned earlier, the dimeric forms of the carboxylic acids are usually assigned the structure

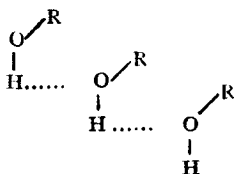


As a consequence of hydrogen bonding, the bond strength of both $\text{C}=\text{O}$ and $\text{O}-\text{H}$ are affected and this is noticed clearly from the shifts in the carbonyl frequencies of Raman spectra^{18, 29} and the carbonyl and hydroxyl frequencies in the infra-red studies of Badger and co-workers.⁵

From the large paramagnetic contribution attached to a double bond, any diminution in the double-bonded character (a decrease in strength of binding) due to hydrogen bonding must lead to a decrease in the Van Vleck paramagnetic term. The observed net increase in diamagnetism is then a clear indication that the dominant factor in this case is presumably the diminished paramagnetism. One can also visualise the ring structure as involving a mobile electron system with a continuously changing bond value throughout the ring. Just as in the case of aromatic ring systems this may result in an increased diamagnetism.¹⁶ The study of anisotropy of the crystalline¹⁷ acids may be expected to throw further light on this aspect of problem. The intramolecular ring structures considered in the earlier section also belong essentially to the same type, a consequence of which is seen in the same molar increase in diamagnetism of one unit per mole. per hydrogen bond.

The principal change in the case of iodic acid from the solid to solution is traceable to a break up of the bifurcated hydrogen bond. This special structure which may be taken to imply a larger electron orbital would naturally lead to an abnormal increase in diamagnetism. It is also possible that the multiplanar system in the unit cell of four molecules constitutes a mobile electron system with the consequent implications.

Contrasted with all these structures, we have the alcohols and water in which the break up of the hydrogen bond leads to an increase in diamagnetism. Structurally the polymers involve only single bonds:



It is generally recognised that every new bond increases the distortion of the electron system, thereby increasing the paramagnetic term while the diminution in the paramagnetic term (factor 2) present in the acids is absent. Possibly, in the case of water and the alcohols the increased paramagnetic term outweighs the diamagnetic term associated with the increased orbitals of the hydrogen bonded system. The apparent difference in behaviour between the two types then becomes understandable.

Interpreted thus, we have to admit that any observed change in susceptibility is determined primarily by the groups involved. This may then be of value in deciding between alternative structures as in the case of methyl formate (*vide* Section 3). From the observed diamagnetic susceptibility, structure II given in that section appears most likely.

7. Summary

A critical analysis of available data shows the constancy of magnetic contribution by the methylene group. Assuming this value it is shown that hydrogen bonding leads to increased diamagnetism, the susceptibility change being one unit per mol whenever structures of the type $O-H \dots O=A$ are involved. A bifurcated hydrogen bond as in iodic acid apparently leads to an even larger value but a proper evaluation of this is at present complicated by other factors. The case of alcohols and water which show a decrease in diamagnetism on association indicates that there is here an increase in the paramagnetic term associated with distortion. The use of this in interpreting structures is indicated.

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