A Semiempirical Theory of Diamagnetic Susceptibilities with Particular Emphasis on Oxygen-Containing Organic Molecules[1]

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Abstract: We present a semiempirical theory of diamagnetic susceptibilities, where the molecular susceptibilities are expressed in terms of contributions of bond and bond–bond interactions. We applied the theory to a series of about 100 oxygen-containing organic compounds, and we found that it gives a very good account of the experimental values. In particular, the differences in susceptibility between different isomers are satisfactorily described. It is pointed out that the theory may be extended to all other classes of organic compounds.

It is generally known[3] that the diamagnetic susceptibilities of many organic compounds may be predicted theoretically by assuming that they are more or less additive. It has been shown for various homologous series of organic compounds that the molar susceptibilities of the compounds in one such series is a linear function of the number of methylene groups. The addition of a CH_2 group seems to increase the molar susceptibility by an amount that varies between -11.2 and -11.9×10^{-6} cgs unit, depending on the type of compounds considered and on the experimental values used.

It is not surprising that various attempts have been made to derive semiempirical theories for the diamagnetic susceptibilities of organic molecules. The best known of these theories was the one proposed by Pascal.[4] Here the molar susceptibility of an organic compound is represented as

$$\chi_M = \Sigma n_X \chi_X \tag{1}$$

where the summation is to be performed over all atomic species X in the molecule, n_X is the number of atoms X present, and χ_X is the susceptibility contribution of atom X to the total susceptibility. What it amounts to is that the molar susceptibility χ_M of an organic molecule is written as a sum of atomic contributions, and that it is assumed that these atomic contributions are constants for all different kinds of organic molecules. The Pascal theory has been remarkably successful, especially in comparison with other semiempirical theories. In general it can predict the diamagnetic susceptibility of an organic molecule to within 5 or 10%.

In spite of all the positive features of the Pascal theory we feel that there is still room for improvement. First, the Pascal theory in its original form disregards the effects of variations in bonding. For example, the susceptibility of a doubly bound oxygen atom, as in an aldehyde, is quite different from the contribution of a singly bound oxygen, as in an alcohol. In subsequent work Pascal accounted for these variations by replacing eq 1 by

$$\chi_M = \Sigma n_X \chi_X + \Sigma \lambda_\gamma \tag{2}$$

where λ_γ is a correction which depends on the nature of the bonds between the atoms. Equation 2 gives more accurate predictions than eq 1, but it is a little less simple and it requires a larger number of susceptibility parameters. A second deficiency of the Pascal theory is that it cannot account for the differences in susceptibility between different isomers. Admittedly, these differences are small; for example, the susceptibilities of *n*-heptane, 2-methylhexane, and 2,2-dimethylpentane are -85.24, -86.24, and -86.97×10^{-6}, respectively.[5] However, they are larger than the possible experimental errors and they are of interest if we wish to obtain structural information from susceptibility measurements.

It is natural that attempts have been made to prove the validity of Pascal's semiempirical theory from first principles. Unfortunately, this is not an easy thing to do, because it is necessary to prove that a molecular susceptibility may be expressed as a sum of atomic contributions within an accuracy of about 10%. We feel doubtful of all attempts to prove the validity of Pascal's theory from molecular orbital theory, because the contributions of overlap charges are usually much larger than 10%; and any theory where these overlap charges would be neglected cannot constitute a proof of Pascal's rules.[6]

We have argued before[7] that a much more promising line of development is derived from the assumption that a molecular susceptibility may be written as a sum of bond contributions and of correction terms that represent interactions between adjacent bonds. For example, according to this theoretical description,[7] the susceptibilities of methane, ethane, and ethyl alcohol are expressed as

$$\begin{aligned}\chi(CH_4) &= \chi_C + 4\chi_{CH} - 6\chi_{HC:CH}\\ \chi(C_2H_6) &= 2\chi_C + \chi_{CC} + 6\chi_{CH} - 6\chi_{CC:CH} - 6\chi_{HC;CH} \qquad (3)\\ \chi(C_2H_5OH) &= \chi_O + 2\chi_C + \chi_{CO} + \chi_{OH} + \chi_{CC} + 5\chi_{CH} - \chi_{CO;OH} - \chi_{CC;CO} - 2\chi_{OC;CH} - 5\chi_{CC;CH} - 4\chi_{HC;CH}\end{aligned}$$

Here the terms χ_C and χ_O represent the contributions to the susceptibility of the 1s electrons on the carbon and oxygen atoms, respectively; the term χ_{CC} represents the contribution of a pair of electrons in a carbon–carbon

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[2] Supported by the National Science Foundation Undergraduate Research Participation Program.

[3] For example, P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, p 81.

[4] P. Pascal, *Ann. Chim. Phys.*, **19**, 5 (1910); **25**, 289 (1912); *Compt. Rend.*, **147**, 56 (1908); **180**, 1596 (1925), and others.

[5] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949).

[6] H. F. Hameka, *ibid.*, **37**, 3008 (1962).

[7] H. F. Hameka, *ibid.*, **34**, 1996 (1961).

bond; and the terms like $\chi_{\mathrm{CC;CH}}$ represent second-order effects between two pairs of electrons in two bonds which have an atom in common. Even though we did not prove explicitly that all the other contributions to the susceptibility are negligible, we showed that it is reasonable to assume that they are very small. Actually, in writing the expression for $\chi(\mathrm{C_2H_5OH})$ we should have included also the lone pair electrons of the oxygen atom, but we will show that this is not really necessary because the lone pair contributions may be combined with the other oxygen parameters.

We have used the above approach to give a theoretical description of the diamagnetic susceptibilities of the saturated hydrocarbons.[7] At first sight it seems as if we need six parameters to represent the susceptibility of an arbitrary alkane. However, we found that the susceptibility expressions always contain specific combinations of the parameters, and that the susceptibilities of the alkanes may all be expressed in terms of the three parameters *A*, *B*, and *C*, which are defined as

$$\begin{aligned} A &= \chi_{\mathrm{C}} + 4\chi_{\mathrm{CH}} + \chi_{\mathrm{CC;CC}} - 2\chi_{\mathrm{CC;CH}} - 5\chi_{\mathrm{CH;CH}} \\ B &= \chi_{\mathrm{C}} + \chi_{\mathrm{CC}} + 2\chi_{\mathrm{CH}} - \chi_{\mathrm{CC;CH}} - \\ &\qquad 4\chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}} \qquad (4) \\ C &= -\chi_{\mathrm{CC;CC}} + 2\chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}} \end{aligned}$$

We also found that our theory would be equivalent to Pascal's theory if we were to neglect the parameter *C* or all the bond–bond interactions. It seems to us that our theory has two advantages over Pascal's theory. First, it can be justified theoretically from first principles. Second, it accounts for details of chemical structure such as the effects of different bonds and the susceptibility variations among different isomers.

We feel that it may be interesting to investigate how accurate our theory is for a variety of organic compounds, and we have chosen the saturated, oxygen-containing compounds as the subject of this investigation. It should be noted that our theory was derived on the assumption that the charge density within a given type of bond (such as a C–H or a C–O bond) is the same in different molecules and in different positions within a molecule. Hence it seems desirable to limit our considerations to saturated organic molecules. We selected the oxygen-containing compounds because the experimental susceptibilities are known for a large number of them, so that we have sufficient data to present a meaningful analysis.

In the following analysis it will appear that initially we need a large number of parameters to express the molecular susceptibilities. But again, as in the case of the alkanes, the many parameters always occur in specific combinations, and in Table I we have listed all parameters that are used in our analysis. It is interesting to note in each class of compounds the chemical significance of the various parameters. For example, in the case of the alkanes, the susceptibilities of methane, ethane, propane, and butane are expressed as $A + C$, $A + B$, $A + 2B$, and $A + 3B$, respectively. It follows that the parameter *B* represents the addition of a $-\mathrm{CH_2}$ group at the end of a hydrocarbon chain. The susceptibilities of butane and isobutane are found to be $A + 3B$ and $A + 3B + C$, respectively. We found that *C* represents a branching in the hydrocarbon chain and is responsible for isomeric effects. It will appear that similar observations can be made in our subsequent analysis.

Table I. Definitions of Susceptibility Parameters

$A = \chi_{\mathrm{C}} + 4\chi_{\mathrm{CH}} + \chi_{\mathrm{CC;CC}} - 2\chi_{\mathrm{CC;CH}} - 5\chi_{\mathrm{CH;CH}}$

$B = \chi_{\mathrm{C}} + \chi_{\mathrm{CC}} + 2\chi_{\mathrm{CH}} - \chi_{\mathrm{CC;CC}} - 4\chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}}$

$C = -\chi_{\mathrm{CC;CC}} + 2\chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}}$

$D = \chi_{\mathrm{O}} + \chi_{\mathrm{OC}} + \chi_{\mathrm{OH}} - \chi_{\mathrm{CH}} - \chi_{\mathrm{HO;OC}} - \chi_{\mathrm{OC;CC}} - 2\chi_{\mathrm{OC;CH}} + \chi_{\mathrm{CC;CH}} + 2\chi_{\mathrm{CH;CH}}$

$E = -\chi_{\mathrm{OC;CC}} + \chi_{\mathrm{OC;CH}} + \chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}}$

$F = \chi_{\mathrm{O}} + \chi^*_{\mathrm{CO}} - 2\chi_{\mathrm{CH}} - \chi^*_{\mathrm{OC;CH}} - \chi^*_{\mathrm{OC;CC}} + 2\chi_{\mathrm{CC;CH}} + 3\chi_{\mathrm{CH;CH}}$

$G = -\chi^*_{\mathrm{OC;CC}} + \chi^*_{\mathrm{OC;CH}} + 2\chi_{\mathrm{CC;CH}} - 2\chi_{\mathrm{CH;CH}}$

$P = 2\chi_{\mathrm{O}} + 2\chi_{\mathrm{C}} + \chi_{\mathrm{OC}} + \chi^*_{\mathrm{OC}} + \chi_{\mathrm{OH}} + \chi_{\mathrm{CC}} + 3\chi_{\mathrm{CH}} - \chi_{\mathrm{HO;OC}} - \chi^*_{\mathrm{OC;CO}} - \chi_{\mathrm{CC;CO}} - \chi^*_{\mathrm{CC;CO}} - 3\chi_{\mathrm{CC;CH}} - 3\chi_{\mathrm{CH;CH}}$

$H = 2\chi_{\mathrm{O}} + 3\chi_{\mathrm{C}} + 2\chi_{\mathrm{OC}} + \chi^*_{\mathrm{CO}} + \chi_{\mathrm{CC}} + 6\chi_{\mathrm{CH}} - \chi^*_{\mathrm{OC;CO}} - 2\chi_{\mathrm{CC;CO}} - \chi^*_{\mathrm{CC;CO}} - \chi_{\mathrm{CO;OC}} - 2\chi_{\mathrm{CC;CH}} - 3\chi_{\mathrm{CH;CH}}$

$J = \chi_{\mathrm{CC;CH}} - \chi_{\mathrm{CH;CH}} + \chi_{\mathrm{OC;CH}} - \chi_{\mathrm{OC;CC}}$

$I = -\chi^*_{\mathrm{CC;CO}} - \chi_{\mathrm{CH;CH}} + \chi^*_{\mathrm{HC;CO}} + \chi_{\mathrm{CC;CC}}$

Alcohols

We found in the literature the experimental susceptibility values of about 30 alcohols, which we have listed in Table II. They vary from methanol to dodecyl alcohol, and from monohydric to hexahydric compounds. We found that the magnetic susceptibility of every saturated alcohol may be expressed in terms of two new parameters *D* and *E*, as defined in Table I, and in terms of the three parameters *A*, *B*, and *C*, which were used for the alkanes.

In order to show this let us first consider ethyl alcohol. According to the rules that we have described previously, its susceptibility may be expressed as

$$\begin{aligned} \chi(\mathrm{C_2H_5OH}) = {} & \chi_{\mathrm{O}}' + 2\chi_{\mathrm{lp}} + 2\chi_{\mathrm{C}} + \chi_{\mathrm{OH}}' + \\ & \chi_{\mathrm{OC}}' - 2\chi_{\mathrm{lp;OH}} + 2\chi_{\mathrm{lp;OC}} + \chi_{\mathrm{CC}} - \\ & 5\chi_{\mathrm{CC;CH}} - \chi_{\mathrm{OC;CC}} - 5\chi_{\mathrm{CC;CH}} - 4\chi_{\mathrm{CH;CH}} \qquad (5) \end{aligned}$$

where the subscript lp denotes a lone pair of electrons on the oxygen atom. We note that in every alcohol we may make the substitutions

$$\begin{aligned} \chi_{\mathrm{O}} &= \chi_{\mathrm{O}}' + 2\chi_{\mathrm{lp}} \\ \chi_{\mathrm{OH}} &= \chi_{\mathrm{OH}}' - 2\chi_{\mathrm{lp;OH}} \qquad (6) \\ \chi_{\mathrm{OC}} &= \chi_{\mathrm{OC}}' - 2\chi_{\mathrm{lp;OH}} \end{aligned}$$

The contributions of the lone pair electrons may be incorporated in the other parameters and there is no need to consider them explicity. In this way eq 5 reduces to eq 3.

We define the parameter *D* as the difference between the susceptibilities of ethanol and ethane.

$$\begin{aligned} D = {} & \chi(\mathrm{C_2H_5OH}) - \chi(\mathrm{C_2H_6}) = \\ & \chi_{\mathrm{O}} + \chi_{\mathrm{OC}} + \chi_{\mathrm{OH}} - \chi_{\mathrm{CH}} - \chi_{\mathrm{HO;OC}} - \\ & \chi_{\mathrm{OC;CC}} - 2\chi_{\mathrm{OC;CH}} + \chi_{\mathrm{CC;CH}} + 2\chi_{\mathrm{CH;CH}} \qquad (7) \end{aligned}$$

It is easily seen that the susceptibility of every primary alcohol, except methanol, is equal to the susceptibility of the corresponding alkane plus the parameter *D*.

Let us now compare the susceptibilities χ_{IP} and χ_{NP} of isopropyl alcohol and *n*-propyl alcohol, respectively.

Table II. The Molar Diamagnetic Susceptibilities of the Alcohols[j]

Compound		χ_{th}^{I}	χ_{th}^{II}	χ_{exptl}	Ref
Methanol	$A + C + D - E$	22.385	22.25	21.15	*a*
				21.40*	*b*
				21.60	*c*
Ethanol	$A + B + D$	34.332	33.811	33.05	*a*
				33.60*	*b*
				33.552	*c*
n-Propyl alcohol	$A + 2B + D$	45.598	45.194	44.44	*a*
				45.20*	*b*
				45.176	*c*
				47.22	*d*
Isopropyl alcohol	$A + 2B + D + E$	46.861	46.292	45.68	*a*
				45.794*	*c*
				47.63	*d*
n-Butyl alcohol	$A + 3B + D$	56.858	56.577	56.15	*a*
				55.90	*b*
				56.536*	*c*
				58.58	*d*
sec-Butyl alcohol	$A + 3B + D + E$	58.121	57.675	57.30	*a*
				57.688*	*c*
				57.6	*e*
				57.9	*e*
Isobutyl alcohol	$A + 3B + C + D$	57.428	57.497	57.21	*a*
				57.704*	*c*
				59.89	*d*
t-Butyl alcohol	$A + 3B + C + D + 2E$	59.954	59.693	57.42	*a*
n-Pentyl alcohol	$A + 4B + D$	68.118	67.960	67.5*	*f*
sec-Pentyl alcohol	$A + 4B + D + E$	69.381	69.058	69.1	*e*
				69.8*	*e*
Isopentyl alcohol	$A + 4B + C + D$	68.688	68.880	68.96*	*a*
t-Pentyl alcohol	$A + 4B + C + D + 2E$	71.214	71.076	70.9*	*g*
n-Hexyl alcohol	$A + 5B + D$	79.378	79.343	79.20*	*b*
Cyclohexanol	$6B + D + E$	73.583	74.394	73.40*	*b*
4-Methyl-2-pentanol	$A + 5B + C + D + E$	81.211	81.361	80.4	*e*
				82.1*	*e*
4-Heptanol	$A + 6B + D + E$	91.901	91.824	91.5	*e*
				93.5	*e*
2,6-Dimethyl-4-heptanol	$A + 8B + 2C + D + E$	115.561	116.43	116.9	*e*
				117.2	*e*
Octanol	$A + 7B + D$	101.898	102.109	102.65*	*h*
Dodecanol	$A + 11B + D$	146.938	147.641	147.70*	*h*
Glycol	$A + B + 2D$	39.098	38.809	38.80*	*h*
1,4-Butanediol	$A + 3B + 2D$	61.61	61.575	61.5*	*i*
2,4-Pentanediol	$A + 4B + 2D + 2E$	75.404	75.154	70.4	*e*
				74.4*	*e*
Hexamethyl glycol	$A + 5B + 2D$	84.138	84.341	84.30*	*b*
Glycerol	$A + 2B + 3D + E$	56.381	56.288	57.06*	*b*
Erythritol	$A + 3B + 4D + 2E$	73.664	73.767	73.80	*b*
Adonitol	$A + 4B + 5D + 3E$	90.947	91.246	91.30*	*b*
Sorbitol	$A + 5B + 6D + 4E$	108.23	108.725	107.80	*b*
Dulcitol	$A + 5B + 6D + 4E$	108.23	108.725	112.40	*b*
Mannitol	$A + 5B + 6D + 4E$	108.23	108.725	111.20	*b*

[a] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, 39, 190 (1943). [b] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949). [c] L. Sacconi and R. Cini, *Atti Accad. Naz. Lincei Rend.*, **16**, 237 (1954). [d] V. G. G. Trew and G. M. C. Watkins, *Trans. Faraday Soc.*, **29**, 1310 (1933). [e] N. Pacault and G. Séris, *Compt. Rend.*, **224**, 1353 (1947). [f] G. Meslin, *Ann. Chim. Phys.*, 7, 145 (1906). [g] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929. [h] B. Cabrera and H. Fahlenbrach, *Z. Physik.*, **85**, 568 (1933). [i] M. Séguin, *Compt. Rend.*, **228**, 839 (1949). [j] The experimental values with an asterisk are the ones that are used for deriving the parameter values.

We have

$$\chi_{IP} = \chi_O + 3\chi_C + \chi_{CO} + \chi_{OH} + 2\chi_{CC} + 7\chi_{CH} - \chi_{CO;OH} - 2\chi_{OC;CC} - \chi_{OC;CH} - \chi_{CC;CC} - 8\chi_{CC;CH} - 6\chi_{CH;CH} \quad (8)$$

$$\chi_{NP} = \chi_O + 3\chi_C + \chi_{CO} + \chi_{OH} + 2\chi_{CC} + 7\chi_{CH} - \chi_{CO;OH} - \chi_{OC;CC} - 2\chi_{OC;CH} - \chi_{CC;CC} - 9\chi_{CC;CH} - 5\chi_{CH;CH}$$

The parameter E is defined as the difference between the above two susceptibilities, namely

$$E = \chi_{IP} - \chi_{NP} = -\chi_{OC;CC} + \chi_{OC;CH} + \chi_{CC;CH} - \chi_{CH;CH} \quad (9)$$

We found that a secondary hydroxyl group is represented by a parameter $D + E$ and a tertiary hydroxyl group by a parameter $D + 2E$; in the case of methanol the hydroxyl group is represented by $D - E$.

In Table II we listed the experimental diamagnetic susceptibilities of the alcohols which we found in the literature. In our first calculation we made use of the parameter values A, B, and C which we derived previously;[6] they are listed in the first column of Table VI. The parameter values of D and E were then derived by following the method of least-squares deviations. Their values are listed in the second column of Table VI, and the resulting theoretical susceptibility values are denoted by a superscript (I) and listed in Table II. We felt that it might be interesting also to repeat the calculation while varying all five parameters. The results are denoted by a superscript (II) in Table II, and the parameter values are listed in the third column of Table VI.

In choosing the experimental susceptibilities which we used for the determination of the parameters, it was often necessary to select one experimental value out of a group of three or four. Also, we excluded some compounds from this calculation if it appeared that they exhibit too large a difference between their theoretical and experimental susceptibilities, especially when we felt some doubt about the accuracy of the experimental results. We felt that these values would have a disproportionate effect on the parameter values and, consequently, we derived the parameter values from the set of experimental data that are denoted in Table II by an asterisk. Ultimately, we reported the theoretical susceptibilities for all compounds listed in Table II.

It may be seen that, in general, the agreement between the experimental and theoretical susceptibilities is quite satisfactory; and it should be noted that the small susceptibility differences between various isomers seem to be properly accounted for by our theory. The largest deviations (4% in one case) are found in the group of hexahydric alcohols, sorbitol, dulcitol, and mannitol. Here our theory predicts the same susceptibility values for all three compounds, while the experimental values vary by as much as 5%. It may be that the experimental values for the above three compounds are unreliable because of the difficulty in seperating them. Otherwise we are forced to conclude that these compounds exhibit small variations in the charge densities of their bonds, caused by the positioning of the OH groups and the curling up of the carbon chain.

Aldehydes and Ketones

The theoretical description of the aldehydes and ketones is very similar to the alcohols, perhaps even a bit simpler. In order to illustrate our method let us consider propionaldehyde and acetone; their susceptibilities, χ_{PR} and χ_{AC}, respectively, are expressed as

$$\chi_{PR} = \chi_O + \chi^*_{OC} + 3\chi_C + 2\chi_{CC} + 6\chi_{CH} - \chi^*_{OC;CC} - \chi^*_{OC;CH} - \chi_{CC;CC} - 8\chi_{CC;CH} - 4\chi_{CH;CH} \tag{10}$$

$$\chi_{AC} = \chi_O + \chi^*_{OC} + 3\chi_C + 2\chi_{CC} + 6\chi_{CH} - 2\chi^*_{OC;CC} - \chi_{CC;CC} - 6\chi_{CC;CH} - 6\chi_{CH;CH}$$

Here we have used asterisks to denote a C═O double bond, in contrast with a C—O single bond. Again, it is not necessary to consider explicitly the contributions of the oxygen lone pair electrons, since they are taken to be incorporated in the other parameters. We compare the expressions of eq 10 with the susceptibility expression of propane

$$\chi(C_3H_8) = 3\chi_C + 2\chi_{CC} + 8\chi_{CH} - \chi_{CC;CC} - 10\chi_{CC;CH} - 7\chi_{CH;CH} \tag{11}$$

This enables us to define the parameter F as the difference between χ_{PR} and $\chi(C_3H_8)$

$$F = \chi_{PR} - \chi(C_3H_8) = \chi_O + \chi_{OC}^* - 2\chi_{CH} - \chi^*_{OC;CH} - \chi^*_{OC;CC} + 2\chi_{CC;CH} + 3\chi_{CH;CH} \tag{12}$$

We found that the susceptibilities of all aldehydes are derived from the corresponding alkane by adding a parameter F for each COH group.

The parameter G is defined as the difference between χ_{AC} and χ_{PR}

$$G = \chi_{AC} - \chi_{PR} = -\chi^*_{OC;CC} + \chi^*_{OC;CH} + 2\chi_{CC;CH} - 2\chi_{CH;CH} \tag{13}$$

It is then found that each ketonic C═O group is represented by a term $F + G$.

In Table III we have listed all available experimental data and our theoretical results for the aldehydes and ketones. The parameter values are listed in Table VI. We followed the same procedure as in the case of the alcohols; *i.e.*, the experimental values with an asterisk are the ones that we used to determine the parameters. In our calculations we made use of the parameter values of A, B, and C that we derived from the alkanes.[7] There did not seem to be any reason for repeating the calculation while varying all five parameters, because it is easily seen that this would not change the agreement between theory and experiment.

It may be seen from Table III that the agreement between theory and experiment is not quite as satisfactory as in the case of the alcohols. We find deviations of about 6% for all the sugars, a 5% difference for 4-hydroxybutanone, and a very large discrepancy of about 50% for formaldehyde. In all other cases the agreement between theory and experiment is satisfactory. The poor agreement for 4-hydroxybutanone is probably due to a lack of accuracy in the experimental value. In the case of the sugars, we suspect that ring closure causes changes in charge density in the various bonds and that this effect is responsible for the differences between the theoretical and experimental values.

We can offer no satisfactory explanation for the large discrepancy in the case of formaldehyde. The experimental work from which we derived the value[8] seems to be quite reliable. However, we may speculate that the facility with which formaldehyde can form trioxane or formaldehyde hydrate might be responsible for the large difference between the value that we predict for formaldehyde and the experimental value that was reported.[8]

Carboxylic Acids

The available experimental magnetic susceptibilities of the carboxylic acids are all listed in Table IV. In order to describe them theoretically it is most convenient to introduce parameter P, which is equal to the magnetic susceptibility of acetic acid.

$$P = 2\chi_O + 2\chi_C + \chi_{OC} + \chi^*_{CO} + \chi_{OH} + \chi_{CC} + 3\chi_{CH} - \chi_{HO;CO} - \chi^*_{OC\ CO} - \chi_{CC;CO} - \chi^*_{CC;CO} - 3\chi_{CC;CH} - 3\chi_{CH;CH} \tag{14}$$

We found that the susceptibilities of all the other carboxylic acids, with the exception of formic acid, can then be expressed interms of the parameters A, B, C, and P.

Formic acid was not included in our theoretical description of the carboxylic acids, but we discovered later that its susceptibility may be expressed in terms

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(8) G. Meslin, *Ann. Chim. Phys.*, 7, 145 (1906).

Table III. The Molar Diamagnetic Susceptibilities of the Aldehydes and Ketones[i]

Compound		χ_{th}	χ_{exptl}	Ref
Formaldehyde	$A + C + F - G$	12.680	18.6	*a*
Acetaldehyde	$A + B + F$	23.548	22.70*	*b*
Propionaldehyde	$A + 2B + F$	34.808	34.32*	*b*
n-Butyraldehyde	$A + 3B + F$	46.068	46.08*	*b*
Isobutyraldehyde	$A + 3B + C + F$	46.638	46.38*	*b*
			47.29	*c*
Isovaleraldehyde	$A + 4B + C + F$	57.898	57.5*	*d*
n-Hexaldehyde	$A + 5B + F$	68.588	69.40*	*b*
Diethylacetaldehyde	$A + 5B + C + F$	69.158	70.71	*b*
Glucose	$A + 5B + 5D + 3E + F + G$	96.357	102.60	*e*
Mannose	$A + 5B + 5D + 3E + F + G$	96.357	102.90	*e*
Galactose	$A + 5B + 5D + 3E + F + G$	96.357	103.00	*e*
n-Heptaldehyde	$A + 6B + F$	79.848	81.02*	*b*
Acetone	$A + 2B + F + G$	34.988	33.96*	*b*
			33.78	*c*
			33.80	*e*
Methyl ethyl ketone	$A + 3B + F + G$	46.248	45.60*	*b*
			45.58	*c*
4-Hydroxybutanone	$A + 3B + D + F + G$	51.008	48.5	*f*
Acetylacetone	$A + 4B + 2F + 2G$	51.658	54.88	*g*
Diethyl ketone	$A + 4B + F + G$	57.508	57.32*	*b*
			58.14	*c*
Methyl *n*-propyl ketone	$A + 4B + F + G$	57.508	57.41*	*b*
Methyl isopropyl ketone	$A + 4B + C + F + G$	58.078	58.45*	*b*
Cyclohexanone	$6B + F + G$	61.710	62.04*	*c*
Methylacetylacetone	$A + 5B + C + 2F + 2G$	63.488	65.0	*d*
Acetonylacetone	$A + 5B + 2F + 2G$	62.918	62.51*	*g*
Methyl butyl ketone	$A + 5B + F + G$	68.768	69.1*	*d*
Methyl isobutyl ketone	$A + 5B + C + F + G$	69.338	69.3*	*h*
Methyl *t*-butyl ketone	$A + 5B + 3C + F + G$	70.478	69.86*	*b*
Methyl *n*-propyl ketone	$A + 5B + F + G$	68.768	69.03*	*b*
Fructose	$A + 5B + 5D + 3E + F + G$	91.357	102.60	*e*
n-Butyl ethyl ketone	$A + 6B + F + G$	80.028	80.73*	*b*
n-Amyl methyl ketone	$A + 6B + F + G$	80.028	80.50*	*b*
Di-*n*-propyl ketone	$A + 6B + F + G$	80.028	80.45*	*b*
Diisopropyl ketone	$A + 6B + 2C + F + G$	81.168	81.14*	*b*
Dimethylcyclohexanone	$8B + 2C + F + G$	85.370	84.8*	*d*
Methyl hexyl ketone	$A + 7B + F + G$	91.288	92.07	*b*
			91.42*	*c*
Diisobutyl ketone	$A + 8B + 2C + F + G$	103.688	104.30*	*b*
Di-*t*-butyl ketone	$A + 8B + 4C + F + G$	104.828	104.06*	*b*

[a] G. Meslin, *Ann. Chim. Phys.*, **7**, 145 (1906). [b] W. R. Angus, G. I. W. Llewelyn, and G. Scott, *Trans. Faraday Soc.*, **51**, 241 (1955). [c] C. M. French and D. Harrison, *J. Chem. Soc.*, 3513 (1955). [d] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929. [e] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949). [f] J. Wiemann and P. Maitte, *Bull. Soc. Chim. Fr.*, 764 (1947). [g] W. R. Angus and G. I. W. Llewelyn, *Trans. Faraday Soc.*, **51**, 245 (1955). [h] M. Séguin, *Compt. Rend.*, **229**, 928 (1947). [i] The experimental values with an asterisk are the ones that are used for deriving the parameter values.

of the parameters I and J, which will be introduced in the following section in order to describe the esters. We calculated the magnetic susceptibility of formic acid from the values of I and J, and we were pleasantly surprised at the good agreement between the experimental and theoretical values.

There are reasons to suspect that our theoretical description of the carboxylic acids might give less satisfactory results than for the alcohols and the aldehydes. Since we are dealing with acids of various strengths, we might suspect significant variations in the charge densities of the bonds of different acids. We noticed that the substitution of the parameters A, B, and C, which were derived from the alkanes, would lead to a rather poor agreement between theory and experiment, and we felt that it was necessary to vary all four parameters in order to get a reasonable theoretical description. The results that are obtained in this way are listed in Table IV.

The agreement between theoretical and experimental values is much better than we would have expected. We found only one serious discrepancy, namely a 5% difference between the experimental and theoretical susceptibilities of hexahydrobenzoic acid. We see no reason to doubt the accuracy of the experimental value and we are inclined to attribute the discrepancy to the effects of ring closure.

It is interesting to note that the parameter values that we derive in the present treatment differ from the previously derived values. We prefer to postpone the discussion of this phenomenon until the last section of this paper.

Esters

The final category of compounds which we considered is the esters. They are interesting because there is so much experimental information about them. We found experimental susceptibilities of 40 compounds having relatively large variations in structure and molecular size. The most convenient set of parameters for describing the susceptibilities of the esters is listed in Table I as H, I, and J. The susceptibility of an arbitrary ester is then expressed in terms of A, B, C, H, I, and J.

The chemical significance of the above parameters is not quite as straightforward as in the previous cases,

Table IV. The Molar Diamagnetic Susceptibilities of the Carboxylic Acids[j]

Compound		χ_{th}	χ_{exptl}	Ref
Formic acid	$P - B - I - J$	19.563	19.90*	*a*
Acetic acid	P	31.010	31.8*	*a*
			31.54	*b*
			31.72	*c*
			31.9	*d*
			32.01	*e*
Propionic acid	$P + B$	42.935	43.50*	*a*
			43.36	*c*
			43.8	*d*
			43.62	*e*
n-Butyric acid	$P + 2B$	54.860	55.10*	*a*
			55.20	*c*
			55.90	*d*
			55.18	*e*
			55.07	*f*
Isobutyric acid	$P + 2B + C$	55.916	56.06*	*c*
n-Valeric acid	$P + 3B$	66.785	66.85*	*f*
Isovaleric acid	$P + 3B + C$	67.841	67.7*	*g*
n-Caproic acid	$P + 4B$	78.710	78.55*	*c*
			78.14	*f*
Hexahydrobenzoic acid	$P + 6B - A + C$	87.598	83.1	*h*
n-Heptanoic acid	$P + 5B$	90.635	88.6*	*a*
n-Caprylic acid	$P + 6B$	102.560	101.6	*f*
Myristic acid	$P + 12B$	174.110	176.0*	*d*
Palmitic acid	$P + 14B$	197.960	198.6*	*d*
Stearic acid	$P + 16B$	221.810	220.8*	*d*
Oxalic acid (anh)	$2P - A - B$	34.077	33.8*	*i*
			35.6	*e*
Malonic acid	$2P - A$	46.002	46.33*	*e*
Succinic acid	$2P - A + B$	57.927	57.88*	*e*

[a] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949). [b] K. Venkatewarlu and S. Sriraman, *Trans. Faraday Soc.*, **53**, 433 (1957). [c] W. R. Angus and W. K. Hill, *ibid.*, **39**, 190 (1943). [d] M. B. Nevgi, *J. Univ. Bombay*, **7** (3), 74 (1938). [e] C. M. French, *Trans. Faraday Soc.*, **43**, 356 (1947). [f] J. Farquharson and M. V. C. Sastri, *ibid.*, **33**, 1472 (1937). [g] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929. [h] P. Passal, *Compt. Rend.*, **180**, 1596 (1925). [i] P. Rumpf and M. Séguin, *Bull. Soc. Chim. Fr.*, 542 (1950). [j] The parameters with an asterisk were derived from the experimental values.

because the esters have much wider variations in structure. The simplest esters consist of two carbon chains, linked together by a -COO- group. It is relatively easy to see that the addition of a CH_2 group to either chain increases the molar susceptibility by an amount B or $B - C$, depending on the substitution site. The dicarboxylic acids all contain a parameter A. We chose the parameter H as the basis for representing the susceptibility of the -COO- group, and we defined it in such a way that H is more or less equal to the susceptibility of methyl acetate. The parameters I and J are necessary to account for the effects of very short carbon chains; for example, most methyl esters contain the parameter I in their susceptibility expressions, and the formates contain, in addition, the parameter J. From the definitions it may be suspected that I and J are quite small, which is confirmed by the results that we obtained.

Out theoretical results are listed in Table V. They were obtained by adjusting all six parameters, and the parameter values are reported in Table VI. The agreement between theory and experiment is very satisfactory except for two or three compounds where we suspect that the differences are due to a lack of accuracy in the experimental results.

Discussion

We believe that the above results show that our theoretical description of magnetic susceptibilities reproduces the experimental values with a degree of accuracy more or less within the experimental errors. There are a few molecules where the agreement falls outside this range, namely the sugars, some of the hexahydric alcohols, hexahydric benzoic acid, and formaldehyde; but here the discrepancies may be explained from chemical considerations. Altogether we have used eleven parameters to represent the susceptibilities of well over a hundred compounds. The values of the parameters which were derived for each category of compounds are listed in Table VI.

We feel that we derived a sufficient number of consistent results to draw some meaningful conclusions from them. An interesting feature is the variations in the B values which are listed in Table VI. On the one hand, these variations are small enough not to cast much doubt on the validity of the theory. On the other hand, they are large enough to be meaningful. Apparently, the addition of a CH_2 group to a carbon chain of a carboxylic acid causes a larger increment in the diamagnetic susceptibility than the addition of a CH_2 group to an alkane chain, even when the chains are quite long. It seems that the charge clouds on the CH_2 groups are more diffuse in the carboxylic acids than in the alkanes. This seems a reasonable conclusion, because the carboxylic acids are more polar than the alkanes; and polarizability effects may cause expansions in the charge clouds all throughout the molecules. The B value for the alcohols is slightly larger than for the alkanes, and that for the esters is slightly smaller than for the acids, which seems to be consistent with the above argument.

The variations in the parameters A and C are relatively much larger than the variations in B. However,

Table V. Theoretical and Experimental Magnetic Susceptibilities of the Esters

Compound		χ_{th}	χ_{exptl}	Ref
Methyl formate	$H - B - 2I - J$	31.209	31.98*	*a*
Ethyl formate	$H - C - I - J$	43.083	43.55	*a*
			43.00*	*b*
Propyl formate	$H + B - C - I - J$	54.789	55.03*	*a*
n-Butyl formate	$H + 2B - C - I - J$	66.495	65.83*	*c*
Isobutyl formate	$H + 2B - C - J$	66.952	66.79*	*c*
Isoamyl formate	$H + 3B - I - J$	78.490	78.38*	*c*
Methyl acetate	$H - I$	42.437	43.51	*a*
			42.60*	*b*
			42.37	*c*
Ethyl acetate	$H + B - C$	54.311	55.10	*a*
			54.10*	*b*
			54.00	*c*
n-Propyl acetate	$H + 2B - C$	66.071	66.43	*a*
			65.91*	*c*
Isopropyl acetate	$H + 2B - C + I$	66.474	67.04*	*c*
n-Butyl acetate	$H + 3B - C$	77.723	77.47*	*c*
Isobutyl acetate	$H + 3B - C + I$	78.180	78.52*	*c*
n-Amyl acetate	$H + 4B - C$	89.429	89.06*	*d*
Isoamyl acetate	$H + 4B$	89.718	89.40*	*b*
			89.81	*c*
Methyl propionate	$H + B - I$	54.143	54.96	*a*
			54.06*	*c*
Ethyl propionate	$H + 2B - C$	66.017	66.51	*a*
			65.75*	*c*
Propyl propionate	$H + 3B - C$	77.723	77.93*	*a*
Isoamyl propionate	$H + 5B$	101.424	101.73*	*c*
Methyl butyrate	$H + 2B - I$	65.849	66.35	*a*
			65.83*	*c*
Ethyl *n*-butyrate	$H + 3B - C$	77.723	77.73	*a*
			77.43*	*c*
Ethyl isobutyrate	$H + 3B$	78.012	78.32*	*c*
Propyl butyrate	$H + 4B - C$	89.429	89.37*	*a*
Isoamyl *n*-butyrate	$H + 6B$	113.13	113.52*	*c*
Ethyl isovalerate	$H + 4B$	89.718	91.1	*e*
n-Amyl valerate	$H + 7B - C$	124.547	124.55*	*c*
Dimethyl oxalate	$2H - A - B - 2I$	57.081	58.15	*a*
			55.7	*e*
Dimethyl malonate	$2H - A - 2I$	68.787	69.61*	*a*
			69.69	*f*
Dimethyl succinate	$2H - A + B - 2I$	80.493	81.05	*a*
			81.50	*f*
Diethyl oxalate	$2H - A + B - 2C$	80.829	80.52*	*a*
			81.71	*f*
Diethyl malonate	$2H - A + 2B - 2C$	92.535	92.59*	*a*
Dipropyl oxalate	$2H - A + 3B - 2C$	104.241	104.44*	*a*
			105.27	*f*
Diisopropyl oxalate	$2H - A + 3B - 2C + 2I$	105.155	106.02*	*f*
Diethyl succinate	$2H - A + 3B - 2C$	104.241	104.48*	*a*
			105.07	*f*
Butyl diacetate	$2H - A + 3B - 2C$	104.241	103.4*	*g*
Diethyl ethylmalonate	$2H - A + 4B - C$	116.236	115.2*	*h*
Ethyl butyl malonate	$2H - A + 6B - C$	139.648	139.32*	*i*
Ethyl diethyl malonate	$2H - A + 6B + C$	140.226	140.41*	*i*
Ethyl ethylpropyl malonate	$2H - A + 7B + C$	151.932	152.43*	*i*
Ethyl ethylbutyl malonate	$2H - A + 8B + C$	163.638	163.27*	*i*
Diethyl sebacate	$2H - A + 9B - 2C$	174.477	177.0	*e*

[a] C. M. French, *Trans. Faraday Soc.*, **43**, 356 (1947). [b] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949). [c] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, 39, 190 (1943). [d] D. B. Woodbridge, *Phys. Rev.*, **48**, 672 (1935). [e] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929. [f] W. R. Angus and G. Scott, *Trans. Faraday Soc.*, **48**, 680 (1952). [g] M. Séguin, *Compt. Rend.*, **228**, 839 (1949). [h] Y. Sato, *Bull. Chem. Res. Inst. Nonaqueous Solutions, Tohoku Univ.*, **6**, (1), 1 (1956). [i] C. M. French and V. C. Trew, *Trans. Faraday Soc.*, **47**, 365 (1951).

it should be noted that in the two cases of the acids and the esters the parameter A occurs in relatively few compounds and, consequently, its value is quite sensitive to changes in the susceptibility. We feel that the value 18.318, which was derived for the alkanes, is much more reliable than any of the others. From a detailed inspection of the susceptibility measurements, especially those experiments where differences in susceptibility variations between different isomers were measured, we are inclined to feel that C ought to be larger than the value 0.570, derived for the alkanes. However, C is such a small parameter that it is difficult to decide what exactly its value should be. At most we can conclude that C is positive and somewhere between 0.5 and 1.0.

From the definitions of the parameters in Table I it may be seen that some of them, in particular C, G, I, and J, ought to be very small, and this is consistent with what we found. It does not seem profitable to attempt the derivation of numerical values for the bond and bond–bond interaction parameters; there is not enough

Table VI. Values of the Parameters That Were Derived for Various Categories of Compounds

Parameter	Alkanes	Alcohols I	Alcohols II	Aldehydes	Carboxylic acids	Esters
A	18.318		17.430		16.018	16.087
B	11.260		11.383		11.925	11.706
C	0.570		0.920		1.056	0.289
D		4.760	4.998			
E		1.263	1.098			
F				−6.030		
G				0.180		
P					31.010	
H						42.894
I						0.457
J						−0.935

information for an exact calculation, and we feel that attempts at approximation are probably unreliable.

Finally, we feel that our present considerations contain the guidelines for a theoretical description of the diamagnetic susceptibilities of all organic molecules. For practical reasons we have limited the discussion to saturated, oxygen-containing organic compounds, but it is easily seen that similar discussions can be presented for other categories of organic compounds. Because of the accuracy of the theoretical results, so that even small variations in susceptibilities between different isomers are accounted for, we feel that such discussions may lead to an increase in understanding of the details of chemical structure.

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Kinetics of the Decomposition of Tetraborane(10)

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Abstract: The decomposition of tetraborane(10) has been studied at 40, 50, and 60° and at pressures of 37, 73, and 110 Torr at each of these temperatures. The course of the reaction was followed by the periodic analysis of the mixture for tetraborane(10), diborane, pentaborane(9), and pentaborane(11). The reaction is $^3/_2$ order in tetraborane(10) at each temperature and pressure except for the 60° runs at the two lower pressures. In these cases the decomposition appears to be approaching first-order behavior.

Excellent bibliographies of the thermal decomposition of various boron hydrides may be found in several books.[1-5] The studies dealing primarily with the decompositions of tetraborane(10) are those of Pearson and Edwards,[6] Dupont and Schaeffer,[7] and Baylis, Pressley, Gordon, and Stafford.[8]

Pearson and Edwards studied the pyrolysis of tetraborane(10) at temperatures of 60, 80, and 100° and found that the rate of decomposition of tetraborane(10) was first order. Decomposition products were diborane, pentaborane(11), hydrogen, a yellow solid, and lesser amounts of pentaborane(9), decaborane, and hexaborane(12). Copyrolysis of diborane and tetraborane(10) resulted in the production of relatively large amounts of pentaborane(11), and the rate of decomposition of tetraborane(10) appeared to be independent of the concentrations of diborane and of pentaborane(11). These authors suggest that tetraborane(10) decomposes by two simultaneous first order paths involving, respectively, B_3H_7 and B_4H_8 intermediates.

Dupont and Schaeffer studied the decomposition of mixtures of diborane and tetraborane(10) at temperatures 70–90°. The rate of the reaction was first order in tetraborane(10) and independent of the diborane pressure. The study appears to support a mechanism in which B_4H_8 is produced by the loss of hydrogen.

The work of Baylis, *et al.*, differs from the above studies in that the data were obtained by the use of a mass spectrometer. A B_4H_8 fragment was detected in the low-pressure pyrolysis at temperatures from 10 to 285° and nearly all known boron hydrides including decaborane were found. No conventional kinetic analysis of the data obtained in this study is possible.

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