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Abstract

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A New Method for Interpreting the Magnetic Susceptibility of Diamagnetic Organic Compounds

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According to quantum-mechanical theory, the magnetic susceptibility χ of diamagnetic molecules is composed of two terms: the classical Langevin diamagnetism χ_d and the quantum-mechanical Van Vleck paramagnetism χ_p ([1]):

$$\chi = \chi_d + \chi_p = -\frac{Ne^2}{mc^2}\sum_i^k \overline{r_i^2} + N\sum_n \frac{|(n|\mu_z|0)|^2}{W_n - W_0}, \tag{1}$$

where N is Avogadro's number; $\overline{r_i^2}$ is the mean value of the square of the distance of the i-th electron from the precession axis; $(n|\mu_z|0)$ are the diagonal matrix elements of the orbital magnetic moments of the unperturbed state; $W_n - W_0$ are the energy differences of the excited and ground unperturbed states.

On the other hand, according to Pascal' s empirical magnetochemical scheme ([2]),

$$\chi = \sum \chi_A + \sum \lambda_s, \tag{2}$$

where χ_A are negative constants assigned to individual atoms comprising the molecule; λ_s are correction constants (positive or negative) characterizing deviation from additivity due to the presence of one or another structural feature.

There is no explicit correspondence between formulas (1) and (2). In other words, Pascal' s empirical constants χ_A and λ_s do not admit a simple physical interpretation from the standpoint of modern theory. We set ourselves the task of considering the magnetochemistry of diamagnetic organic compounds on the basis of expression (1).

To separate the measured χ into χ_d and χ_p, which cannot be done experimentally, we proceeded as follows. The Langevin diamagnetism of molecules, as being less sensitive to structural features than χ_p, was calculated by Kirkwood' s approximate formula ([3])

$$\chi_d = -\frac{Ne^2 a_0^{2\,1/2}}{4mc^2}\sqrt{k\alpha} = -3.11 \cdot 10^6 \sqrt{k\alpha}, \tag{3}$$

where $a_0 = \hbar^2/mc^2$ is the so-called Bohr radius; k is the total number of electrons in the molecule; α is the experimentally measured polarizability.

Analysis of Kirkwood' s formula and comparison of the calculated susceptibility values with experimental ones for compounds for which one may assume $\chi_p \simeq 0$ clearly show that the approximate formula (3) describes the Langevin diamagnetism of molecules well.

Comparison of the χ_d calculated from (3) with experimental data χ made it possible to estimate χ_p for a large number of aliphatic and alicyclic compounds. Consideration of these data revealed a number of regularities.

First, it was established that the specific carriers of paramag-

of the paramagnetism χ_p– "magnetophores" –are certain groups of atoms, listed in Table 1 together with approximate values of their individual paramagnetic susceptibilities χ'_p.

Table 1

	$>C=C<$	$-C\equiv C-$	$>C=O$	$C(=O)H$	$C(=O)OH$	OH	$C(=O)NH_2$	$-N(=O)O$	$C\equiv N$	$-C(=O)O-$
$+\chi'_p \cdot 10^6$	~ 8	~ 3	~ 11	~ 11	8.2	~ 1	~ 7	15.8	~ 3	~ 9

Secondly, it has been shown that molecules as a whole possess a certain comparatively small total molecular paramagnetism χ''_p, which depends on the symmetry of the molecule and decreases with increasing branching of isomers. Thus,

$$\chi_p = \sum \chi'_p + \chi''_p. \tag{4}$$

The summation of the paramagnetism of individual magnetophoric groups is fully valid only when they are located far from one another in the molecule (for example, diallyl).

Thirdly, it has been shown that an additive scheme can be applied to the diamagnetic component of the susceptibility χ_d. It then turns out that individual atoms can be assigned atomic diamagnetic components: $\chi'_{dC} = -8 \cdot 10^{-6}$, $\chi'_{dH} = -2 \cdot 10^{-6}$, $\chi'_{dO} = -9 \cdot 10^{-6}$, $\chi'_{dN} = -7 \cdot 10^{-6}$, $\chi'_{dCl} = -19 \cdot 10^{-6}$, etc. The presence of double and triple bonds $C = C$, $C \equiv C$, etc. appears as a small excess diamagnetism, analogous to refraction exaltation: $\chi'_{dC=C} \simeq -1.6 \cdot 10^{-6}$,

$\chi'_{dC\equiv C} \simeq -1.8 \cdot 10^{-6}$, etc. All these constants, both atomic and group constants, have a definite physical meaning, in which they differ substantially from Pascal' s empirical constants. Thus, we have developed a new magnetochemical scheme, in agreement with formula (1). For practical application of this scheme to determining structural formulas of organic compounds, it is not necessary painstakingly to calculate the diamagnetic component χ_d according to the indicated additive scheme. For this task it is simpler to use (in the case of aliphatic or alicyclic compounds) Kirkwood' s formula (3). The susceptibility of a compound is then calculated as follows:

$$\chi = -3.11 \cdot 10^6 \sqrt{k\alpha} + \sum \chi'_d + \sum \chi'_p + \chi''_p, \tag{5}$$

Table 2

	$-\chi \cdot 10^6$calc. by our scheme*	$-\chi \cdot 10^6$exp.	$-\chi \cdot 10^6$calc. by the new Pascal scheme
Glycol	38.5—39.5	38.7; 39.0	37.4
Allyl alcohol	36.2—36.7	36.7	34.0
Oleic acid	210.3	208.0; 209.5	208.3

* χ''_p for oleic acid was extrapolated for 14 CH_2 groups; for the others it was taken from experiment for one CH_2 group.

where α is measured experimentally; k is determined directly from the composition; χ'_p are taken from Table 1.

Table 2 gives, as an example, susceptibility values for several compounds calculated by our scheme (5), as well as experimental data and values calculated by the new Pascal scheme. The comparison shows that our scheme, being physically unambiguous, at the same time is not inferior to Pascal' s scheme in other respects. The additive scheme for the diamagnetic component may find application for calculations of intramolecular fields, as will be reported in article ([4]).

REFERENCES

1. J. H. Van-Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1948.

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4. Ya. G. Dorfman, DAN, **119** No. (1958).

Note: Figure translations are in progress. See original paper for figures.