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Abstract

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On the Relation between the Number of π-Electrons and the Character of the Magnetic Susceptibility of One Class of Aromatic Molecules

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In the one-electron approximation, the contribution χ_π, made by interatomic π-electron currents to the magnetic susceptibility of an aromatic molecule, may be represented in the form:

$$\chi_\pi = \sum_p \nu_p \chi_p = -\sum_p \nu_p \left(\frac{\partial^2 \varepsilon_p}{\partial H^2} \right)_{H=0} ; \tag{1}$$

$\nu_p = 0, 1,$ or 2 is the number of π-electrons on the p-th molecular energy level ε_p. In the molecular-orbital method (1), the dependence of ε_p on the intensity of a homogeneous magnetic field H, perpendicular to the plane of the molecule, is determined from the condition that the determinant of the matrix W, whose elements have the form

$$W_{kl} = (\alpha - \varepsilon)\delta_{kl} + \eta_{kl}\beta \exp\left(\frac{ie}{hc} H S_{kl} \right). \tag{2}$$

is equal to zero. The indices k and l number the atoms in the conjugated system; α and β are the usual "Coulomb" and "resonance" integrals in the molecular-orbital method; δ_{kl} is the Kronecker symbol; $\eta_{kl} = 1$ for neighboring atoms and $\eta_{kl} = 0$ for non-neighboring atoms k and l; S_{kl} is the area of the triangle whose vertices are located at an arbitrarily chosen origin of coordinates and at the k-th and l-th atoms.

Thus, for example, for a monocyclic aromatic molecule in which the conjugated bonds form a cycle with $2N$ links enclosing an area S, the molecular energy levels in a magnetic field are determined by the equation:

$$\varepsilon_p = \alpha + 2\beta \cos \frac{1}{N} \left(\pi p \pm \frac{eHS}{2hc} \right), \quad \text{where } p = 0, 1, \ldots, N. \tag{3}$$

It follows from (3) that in the absence of a magnetic field (at $H = 0$) all energy levels (with the exception of the very lowest and the very highest) in a monocyclic aromatic molecule are doubly degenerate. Differentiation of formula (3) with respect to H gives:

$$\chi_p = -\left(\frac{\partial^2 \varepsilon_p}{\partial H^2}\right)_{H=0} = \frac{e^2 S^2 \beta}{2N^2 \hbar^2 c^2} \cos\frac{p\pi}{N}. \tag{4}$$

Since $\beta < 0$, for occupied energy levels ($p \leq N/2$) one has $\chi_p < 0$. This means that the interatomic π-electron current induced by a magnetic field in the electron cloud of each occupied molecular orbital, in the case of a monocyclic aromatic molecule, is diamagnetic in character.

However, in the case of polycyclic aromatic molecules the quantities χ_p vary not only in magnitude but also in sign: they may be either diamagnetic or paramagnetic. In accordance with the usually observed enhanced diamagnetic susceptibility of aromatic molecules in the direction perpendicular to the plane of the system of conjugated bonds, in most cases the diamagnetic values χ_p predominate. For some aromatic molecules, however, calculation leads to paramagnetic values of χ_π ($\chi_\pi > 0$). Such molecules must be characterized with reduced diamagnetic (or even a certain paramagnetic) susceptibility in the direction perpendicular to the plane of the molecule.

Up to the present time there has been no analysis of the conditions under which the total contribution of interatomic π-electron currents χ_π to the magnetic susceptibility of a molecule is not diamagnetic but paramagnetic in character.

For a qualitative clarification of this question it is convenient to use perturbation theory. Expanding in (2) the exponential function in a series and using the usual formulas of perturbation theory, we have

$$\chi_p = \chi_p^{(1)} + \chi_p^{(2)} = \frac{e^2 \beta}{\hbar^2 c^2} \sum_{k,l} \left(c^*_{pk} c_{pl} + c^*_{pl} c_{pk}\right) S^2_{kl} \eta_{kl} - \frac{2e^2 \beta^2}{\hbar^2 c^2} \sum_{q \neq p} \frac{\left|\sum_{k,l} \left(c^*_{qk} c_{pl} - c^*_{ql} c_{pk}\right) S_{kl} \eta_{kl}\right|^2}{\varepsilon_p - \varepsilon_q}; \tag{5}$$

c_{pk} denotes the coefficient of the π_z-function of the k-th atom in the expression for the p-th molecular orbital.

Let us now turn to the case of aromatic molecules for which the spectrum of energy levels in the absence of a magnetic field may be regarded as the result of a doublet splitting of the degenerate levels of a monocyclic aromatic molecule (see formula (3) for $H = 0$) under the action of some nonmagnetic perturbation. Under the condition that the doublet splitting is small, it follows from the form of the denominators in the second term of expression (5) that the principal contribution to the value of $\chi_p^{(2)}$ for an energy level that is a sublevel of some doublet is made by the term corresponding to the transition between this sublevel and the other sublevel of the same doublet. In this case the principal terms in the expressions for $\chi_p^{(2)}$ for the different sublevels of one and the same doublet differ only in sign, so that the sum of the values $\chi_p^{(2)}$, calculated for the two sublevels of a doublet completely occupied by electrons, is small in comparison with the reciprocal value of the doublet splitting. At the same time, under the condition that the doublet splitting is small, for each separate sublevel the magnitude of $\chi_{(p)}^{(2)}$ exceeds $\chi_p^{(1)}$ in absolute value. This means that the sum of the quantities $\chi_p^{(1)}$ and $\chi_p^{(2)}$ is diamagnetic for the upper and paramagnetic for the lower sublevel of a doublet: the signs of the magnetic susceptibilities of the π-electrons on doublet sublevels alternate.

On the basis of these qualitative considerations it is not difficult to establish the relation between the number of π-electrons and the character of the quantity χ_π for an aromatic molecule possessing an energy spectrum of the type considered here. If the number of π-electrons is equal to $n = 4m + 2$, then all pairs of doublet levels are either completely occupied or completely empty. In summing over the individual sublevels of the doublets, the larger, in absolute value, contributions of the quantities $\chi_p^{(2)}$ compensate one another, and the quantity χ_π for the molecule is diamagnetic (as in an unperturbed monocyclic molecule). If, however, $n = 4m$, then in one of the doublets only the lower sublevel is occupied by electrons, making a large uncompensated paramagnetic contribution to the quantity χ_π.

Thus, aromatic molecules possessing an energy spectrum of the type considered are divided into two groups: 1) molecules with "normal" diamagnetic π-electron susceptibility ($n = 4m + 2$), and 2) molecules with "anomalous" (reduced diamagnetic or even a certain paramagnetic) π-electron susceptibility ($n = 4m$).

These conclusions, in particular, apply to aromatic molecules in which the system of conjugated bonds consists of one chain of fused polygons (with all atoms belonging to the conjugated system lying on the contour of the molecule). To this class belong molecules of polyacenes and molecules obtained from the latter by the formal replacement of six-membered rings by rings with a different number of members (for example, 4, 5, or 7). If internal bonds are neglected, the molecules under consideration pass into

monocyclic and (according to (3)) possess degenerate energy levels in the absence of a magnetic field. The presence of internal bonds leads to a doublet splitting of the degenerate levels.

Table 1

Relative magnitudes of the contributions χ_π made by interatomic π-electron currents to the magnetic susceptibility of aromatic molecules

Molecule	Number of π-electrons n	Theoretical values* I	Theoretical values* II	Theoretical values* III	Experimental values χ_π
Molecules with “normal” π-electron magnetic susceptibility ($n = 4m + 2$)					
Benzene	6	1	1	1	1
Naphthalene	10	2.19	2.22	2.01	2.06—2.11
Azulene	10	2.26	2.27	2.14	2.38
Anthracene	14	3.45	3.53	3.08	3.23—3.38
Naphthacene	18	4.75	4.88	–	–
Pentacene	22	6.06	6.26	–	–
Molecules with “anomalous” π-electron magnetic susceptibility ($n = 4m$)					
Pentalene	8	−2.78	−2.53	−2.84	–
Heptalene	12	−8.34	−0.93	−9.50	–
Biphenylene	12	−0.13	−0.17	–	–
Dibenzopentalene	16	−0.75	−0.46	–	–
Dibenzo-2,3—7,8-heptalene	20	–	−4.17	–	–
Dibenzo-1,—26,7-heptalene	20	–	−3.57	–	–

* The theoretical values of χ_π were obtained: I —by the molecular-orbital method, neglecting the nonorthogonality integrals (with $S = 0$); II —by the same method with $S = 0.25$; III —by means of the branched free-electron model.

Table 1 gives data on the magnitudes of χ_π for a number of aromatic molecules of the class under consideration, fully confirming the formulated rule on the dependence of the character of the quantity χ_π on the number of π-electrons in the molecule. In particular, it has now become clear why azulene, which has 7- and 5-membered rings, is close in its magnetic properties to naphthalene, and not to pentalene or heptalene, which have, respectively, two 5- or 7-membered rings.

Since the attachment of a benzene ring to an aromatic molecule of the class under consideration increases the number of its π-electrons by 4, this does not transfer the molecule from one group to the other. For this reason, benzene and polyacenes, azulene and its benzologues belong to the group of "normal" molecules, while pentalene, heptalene, biphenylene, and their benzologues belong to the group of "anomalous" molecules. Since, however, the attachment of benzene rings increases the number of completely filled doublet levels in the molecule, this leads to an increase in the total diamagnetic contribution made by such levels to the magnetic susceptibility of the molecule. For this reason, for example, the anomalies of the π-electron magnetic properties of the benzologues of pentalene and heptalene should be less sharply expressed than in the parent molecules.

In conclusion, we note that the formulated rule can be used to predict the character of the magnetic properties of the π-electrons of new aromatic molecules of the class under consideration.

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

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