

## $\pi$ -Electron Ring Currents and Magnetic Properties of Porphyrin Molecules in the MO LCAO SCF Method

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The coupled variant of double-parameter perturbation theory in the MO LCAO SCF method in the London approximation has been used for the calculation of  $\pi$ -electron current distributions in the molecules of porphyrin and its derivatives. The chemical shifts of  $^1\text{H}$ -NMR have been computed on the basis of calculations of ring currents and charge distributions. It is shown that  $\pi$ -electron ring currents are responsible for the dominant contribution to the shielding of protons. The theoretical and experimental values of proton chemical shifts are in a good agreement. Chemical shifts of the  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclei have also been estimated. Two aromaticity scales are proposed for the compounds under study based on the calculations of the  $\pi$ -electron contribution to the diamagnetic susceptibility and of  $\pi$ -electron currents, respectively.

**Key words:** Porphyrins – Ring currents – Chemical shifts – Diamagnetic shielding.

### 1. Introduction

It is a common practice to relate the peculiar magnetic properties of cyclic conjugated molecules, namely higher anisotropy of diamagnetic susceptibility along the axis normal to the molecular plane and the range of proton magnetic resonance spectra different from those of their acyclic analogs, to the Larmor precession of delocalized  $\pi$ -electrons, i.e. to the induced  $\pi$ -electron ring currents

first introduced by Pauling [1]. The question of the reality of the  $\pi$ -electron currents was discussed time and again [2–7]. The applicability of the ring current model to the porphyrin series is the strongest evidence of its validity. An extremely wide range of the  $^1\text{H}$ -NMR spectra of these compounds ( $\sim 15$  ppm) observed experimentally [8, 9] is readily explained by the shielding and deshielding effects of the  $\pi$ -electron ring currents exerted on internal and external protons of the tetrapyrrole macrocycle. Starting from the pioneer  $^1\text{H}$ -NMR studies [10, 11], various ring current model modifications such as: the point dipole model (single-loop model) [12], double-loop model [13, 14], “network” model in which the molecule was considered as a network, electromotive force induced in the circuit was assumed to be proportional to the network area and the resistance was assumed to be proportional to the number of bonds [15] and others were widely used for theoretical treatment of the NMR spectra. The agreement between the experimental values of the chemical shifts and those calculated by using these semiclassical models, though it was qualitative, supported first of all the idea of the existence of induced ring currents (see, for example, [16]).

The quantum mechanical description of induced currents developed by London [17], McWeeny [18] and Pople [19] on the basis of Hückel approximation made it possible not only to improve the methods of the current calculation but also to calculate more correctly the magnetic shielding and to give, in particular, more reasonable values of the proton chemical shifts of porphyrin molecules [20]. This technique is based on the use of gauge invariant atomic orbitals introduced by London and is distinctive for its relative simplicity promoting its wide application. At the same time it possesses some shortcomings, the neglect of electron–electron interaction being the most pronounced.

A consistent quantum mechanical calculation of the properties of a molecule in the external magnetic field is based on one of the variants of perturbation theory. In this case the tensors of magnetic shielding and diamagnetic susceptibility are determined from the molecule energy corrections which are proportional to the product of the nuclear magnetic moment and the uniform magnetic field strength, and to the latter squared, respectively. Such an approach is equivalent to the description of the magnetic properties of molecules in terms of the electron currents with the density  $\mathbf{j}(\mathbf{r})$  induced by the applied magnetic field provided the density is understood as the quantum mechanical average of the appropriate operator calculated using the perturbed wave functions. In Ref. [21], (see also Ref. [22]) using a coupled variant of perturbation theory in the MO LCAO SCF method in the London approximation the matrix of the induced  $\pi$ -electron currents  $I$  has been introduced by which the  $\pi$ -electron contributions to the diamagnetic susceptibility and magnetic shielding are expressed. Also, it has been shown that in the London approximation the first Kirchhoff law for the elements  $I_{pq}$  is fulfilled only if the coupled variant of perturbation theory of the MO LCAO SCF is used (as in the case of the Hückel approximation). The uncoupled variant (as was shown in studies [23]) and the geometric approximation [24] are not gauge invariant, and within the framework of these schemes the  $\pi$ -electron ring currents have no physical meaning [21] since here the first Kirchhoff law does not hold.

In the present work the coupled variant of the perturbation theory of the MO LCAO SCF method in the  $\pi$ -electron approximation earlier verified in calculations of the diamagnetic susceptibility and magnetic shielding of protons and of the  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclei for a series of alternant and non-alternant hydrocarbons, their ions and nitrogen-containing heteroaromatic compounds [22, 25–29], is used to describe the charge and current distributions in the molecules of porphyrin and a number of its derivatives.

## 2. Calculation Method

The consistent consideration of the electron–electron interaction, when calculating the magnetic properties of molecules by the Hartree–Fock method, leads to the coupled variant of double-parameter perturbation theory the small parameters of which are the applied homogeneous magnetic field  $\mathbf{H}$  and the magnetic moment of a nucleus  $\boldsymbol{\mu}$  [30–32, 25]. In the MO LCAO method the basic equations for the matrix of  $\pi$ -electron bond orders and residual charges of molecule,  $\mathbf{Y} = 2\mathbf{R} - \mathbb{1}$ , the involutory analogue of the reduced first order density matrix ( $\mathbf{R}$  is the McWeeny density matrix,  $\mathbb{1}$  is the unit matrix), have the form

$$\mathbf{F}\mathbf{Y} = \mathbf{Y}\mathbf{F}, \mathbf{Y}^2 = \mathbb{1} \quad (1)$$

where  $\mathbf{F} = \mathbf{H} + \mathbf{G}(\mathbf{Y})$  is the matrix of the Fock operator,  $\mathbf{H}$  is the matrix of the interaction of the  $\pi$ -electrons with the screened  $\sigma$ -core of the molecule,  $\mathbf{G}(\mathbf{Y})$  is the matrix of the averaged electron–electron interactions

$$[\mathbf{G}(\mathbf{Y})]_{st} = \sum_{pq} \mathbf{Y}_{pq} \{ [sp | tq] - \frac{1}{2}[sp | qt] \} \quad (2)$$

and  $[sp | tq]$  are the integrals of electron–electron interaction.

Expanding the matrices  $\mathbf{F}$  and  $\mathbf{Y}$  in power series in the small parameters of the perturbation,

$$\mathbf{F} = \sum_{\alpha\beta} \sum_{ij} \mathbf{F}_{\alpha\beta}^{ij} \mathbf{H}_{\alpha\beta}^i \boldsymbol{\mu}_{\beta}^j, \quad \mathbf{Y} = \sum_{\alpha\beta} \sum_{ij} \mathbf{Y}_{\alpha\beta}^{ij} \mathbf{H}_{\alpha\beta}^i \boldsymbol{\mu}_{\beta}^j,$$

and substituting them in (1) we obtain systems of matrix equations for the corresponding corrections to the density matrix. The unperturbed equation is of the same form as (1), and, in particular, for the matrix  $\mathbf{Y}^{10}$  which is actual for the calculation of the diamagnetic susceptibility and magnetic shielding we obtain (the tensor indices  $\alpha, \beta = x, y, z$  are omitted) [33],

$$\begin{aligned} \mathbf{F}^{00}\mathbf{Y}^{10} - \mathbf{Y}^{10}\mathbf{F}^{00} + \mathbf{G}(\mathbf{Y}^{10})\mathbf{Y}^{00} - \mathbf{Y}^{00}\mathbf{G}(\mathbf{Y}^{10}) &= \mathbf{Y}^{00}\mathbf{H}^{10} - \mathbf{H}^{10}\mathbf{Y}^{00}, \\ \mathbf{Y}^{10}\mathbf{Y}^{00} + \mathbf{Y}^{00}\mathbf{Y}^{10} &= 0. \end{aligned} \quad (3)$$

In the  $\pi$ -electron approximation, with the London method [17], the perturbation matrices up to the second order in  $\mathbf{H}$  and  $\boldsymbol{\mu}$  are as follows [30–32, 25]

$$\begin{aligned} \mathbf{H}^{10} &= i\alpha \mathbf{S} \circ \mathbf{H}^{00}, & \mathbf{H}^{20} &= \frac{1}{2}i\alpha \mathbf{S} \circ \mathbf{H}^{10}, \\ \mathbf{H}^{01} &= 2i\alpha \mathbf{S}_\nu \circ \mathbf{K}_\nu \circ \mathbf{H}^{00}, & \mathbf{H}^{11} &= i\alpha \mathbf{S} \circ \mathbf{H}^{01} + \frac{\hbar^2 \alpha}{m\varepsilon} \mathbf{L}_\nu. \end{aligned} \quad (4)$$

Here  $\alpha = e^2/\hbar c$  is the fine structure constant,  $S_{pq} = \frac{1}{2}\mathbf{R}_p \times \mathbf{R}_q$ ,  $(S_\nu)_{pq} = \frac{1}{2}\mathbf{R}_{p\nu} \times \mathbf{R}_{q\nu}$ ,  $(\mathbf{K}_\nu)_{pq} = 8|\mathbf{R}_{p\nu} + \mathbf{R}_{q\nu}|^{-3}$ ,  $(L_\nu)_{pq} = \delta_{pq}|\mathbf{R}_{p\nu}|^{-1}$ ,  $\mathbf{R}_{p\nu} = \mathbf{R}_p - \mathbf{R}_\nu$ ,  $\mathbf{R}_p$  is the radius-vector of the  $p$ th  $\pi$ -electron center,  $\mathbf{R}_\nu$  is the radius-vector of the  $\nu$ th shielded nucleus,  $\epsilon = 1.57$  is the effective dielectric constant of the  $\pi$ -electron cloud, the symbol  $\times$  means the vector product and  $\circ$  denotes the Hadamard matrix product, i.e.  $(\mathbf{A} \circ \mathbf{B})_{pq} = A_{pq}B_{pq}$ . It has been taken into account in Eq. (4) that in the case of planar molecules only components of  $H^{ij}$  along the axis perpendicular to the molecular plane are different from zero.

The methods of numerical solution of Eqs. (1) and (3) are described in Ref. [33], and will not therefore be considered here. We note only that Eqs. (3) must be regarded as a nonhomogeneous linear system for the  $n^2$  matrix elements of  $\mathbf{Y}^{10}$  its solution being equivalent to the representation of  $\mathbf{Y}^{10}$  in the form of superposition of all singly excited and some doubly excited configurations [33].

The formulae for the  $\pi$ -electron contribution to the tensors of diamagnetic susceptibility  $\chi$  and magnetic shielding of the  $\nu$ th nucleus  $\sigma_\nu$ , as well as their averages

$$\chi = (\chi_{xx} + \chi_{yy} + \chi_{zz})/3 \quad \text{and} \quad \delta_\nu = (\sigma_{\nu,xx} + \sigma_{\nu,yy} + \sigma_{\nu,zz})/3$$

are obtained without difficulty from the expansion in a power series in  $\mathbf{H}$  and  $\boldsymbol{\mu}$  of the Hartree-Fock expression for the electronic energy

$$E = \frac{1}{2}\text{Sp} [(1 + \mathbf{Y})(\mathbf{H} + \mathbf{F})] = E^{00} + \sum_{\alpha\beta} \sum_{ij} E^{ij} H_\alpha^i \mu_\beta^j$$

giving [25] (see also [30–32])

$$\chi = -\frac{1}{6}\text{Sp} (\mathbf{Y}^{00}\mathbf{H}^{20} + \frac{1}{2}\mathbf{Y}^{10}\mathbf{H}^{10}) \quad (5)$$

$$\delta_\nu = \frac{1}{3}\text{Sp} (\mathbf{Y}^{00}\mathbf{H}^{11} + \mathbf{Y}^{10}\mathbf{H}^{01}). \quad (6)$$

It should be emphasized that for the calculation of the  $\chi$  and  $\delta_\nu$  values it is sufficient to solve Eqs. (1) and (3) for the matrices  $\mathbf{Y}^{00}$  and  $\mathbf{Y}^{10}$  only [25]. Note also that solving Eq. (3) we avoid the necessity to sum the traditional series of perturbation theory or to use the rough approximation of mean energy.

The formulae (4) through (6) can be obtained by a different route – not on the basis of perturbation theory, but using the formulae of classical electrodynamics with preliminary quantum-mechanical averaging of the current density operator [21],

$$\mathbf{j}(\mathbf{r}) = -\frac{e}{2m} \sum_a \left\{ \left[ \hat{\mathbf{p}}_a + \frac{e}{c}\mathbf{A}(\mathbf{r}) \right] \delta(\mathbf{r} - \mathbf{r}_a) + \delta(\mathbf{r} - \mathbf{r}_a) \left[ \hat{\mathbf{p}}_a + \frac{e}{c}\mathbf{A}(\mathbf{r}) \right] \right\}. \quad (7)$$

Using the technique of Ref. [19] the following expression can be obtained for the current density operator within the framework of the LCAO method in the basis

of gauge-invariant AO's [17]  $\psi_s = \varphi_s(\mathbf{r} - \mathbf{R}_s) \exp(-i\alpha\mathbf{A}_s\mathbf{r})$  (conf. [34]),

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= -\frac{e}{2m} \sum_{st} \{Y_{st}^{00} e^{i\alpha(\mathbf{A}_s - \mathbf{A}_t)\mathbf{r}} (2\mathbf{A} - \mathbf{A}_s - \mathbf{A}_t) \varphi_s^* \varphi_t \\ &\quad + [Y_{st}^{00} e^{i\alpha(\mathbf{A}_s - \mathbf{A}_t)\mathbf{r}} - iY_{st}^{10}] (\varphi_s^* \hat{\mathbf{p}} \varphi_t - \varphi_t^* \hat{\mathbf{p}} \varphi_s)\} \\ &\equiv \sum_{st} \mathbf{j}_{st}(\mathbf{r}). \end{aligned} \quad (8)$$

Here  $\mathbf{A} = \frac{1}{2}(\mathbf{r} \times \mathbf{H})$ ,  $\mathbf{A}_s = \frac{1}{2}(\mathbf{R}_s \times \mathbf{H})$ ,  $\varphi_s$  may be regarded as the atomic orbital in the absence of magnetic field [25],  $\hat{\mathbf{p}}$  is the linear momentum operator.

The tensors of diamagnetic susceptibility of a molecule  $\chi$  and of magnetic shielding of the  $\nu$ th nucleus  $\sigma_\nu$  may be found from the expression for the induced magnetic moment of a molecule and the Biot-Savart-Laplace law

$$\mathbf{M} = \chi \mathbf{H} = \frac{1}{2c} \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) d\tau \quad (9)$$

$$\mathbf{H}' = -\sigma_\nu \mathbf{H} = \frac{1}{c} \int (\mathbf{r} - \mathbf{R}_\nu) \times \mathbf{j}(\mathbf{r}) / |\mathbf{r} - \mathbf{R}_\nu|^3 d\tau. \quad (10)$$

If one substitutes (8) into (9) and (10) and uses the ZDO principle  $\varphi_s^* \varphi_t = \delta_{st} |\varphi_s|^2$  which is usual in the  $\pi$ -electron approximation, then the first item in (8) will give the atomic, or local, contribution to  $\chi$  and  $\sigma_\nu$  and the second item will give the interatomic, or current, contributions.

Thus, the substitution of (8) into (9) gives

$$\begin{aligned} \mathbf{M} &= \chi \mathbf{H} \\ &= -\frac{e}{4mc} \sum_{st} Y_{st}^{00} \int e^{i\alpha(\mathbf{A}_s - \mathbf{A}_t)\mathbf{r}} [\mathbf{r} \times (2\mathbf{A} - \mathbf{A}_s - \mathbf{A}_t)] \delta_{st} |\varphi_s|^2 d\tau \\ &\quad - \frac{e}{4mc} \sum_{st} Y_{st}^{00} \int e^{i\alpha(\mathbf{A}_s - \mathbf{A}_t)\mathbf{r}} [\varphi_s^* (\mathbf{r} \times \hat{\mathbf{p}}) \varphi_t - \varphi_t^* (\mathbf{r} \times \hat{\mathbf{p}}) \varphi_s] d\tau \\ &\quad + \frac{ie}{4mc} \sum_{st} Y_{st}^{10} \int [\varphi_s^* (\mathbf{r} \times \hat{\mathbf{p}}) \varphi_t - \varphi_t^* (\mathbf{r} \times \hat{\mathbf{p}}) \varphi_s] d\tau. \end{aligned} \quad (11)$$

In the London approximation all terms of the first sum in (11) – the local contributions to diamagnetic susceptibility – are zero. The second and third items in (11) – the diamagnetic and paramagnetic contributions to  $\chi$  – transform into (5) with allowance for (4) if: (a) one takes outside the integral sign the mean value of the distance to the electron localized on the bond  $s-t$   $\mathbf{r} \Rightarrow \frac{1}{2}(\mathbf{R}_s + \mathbf{R}_t)$ , (b) one restricts oneself in the first term of the expansion of the exponent in a series, and (c) one uses the Linderberg formula for the matrix elements of the linear momentum operator [35]

$$i\hbar \int \varphi_s^* \hat{\mathbf{p}} \varphi_t d\tau = H_{st}^{00} (\mathbf{R}_s - \mathbf{R}_t). \quad (12)$$

The expression (6) is obtained with allowance for (4) if an analogous procedure is applied to formula (10). When finding the local contribution to  $\sigma_\nu$ , it is necessary to take out the integral sign the mean distance from the shielded nucleus  $\nu$   $r \Rightarrow \frac{1}{2}(\mathbf{R}_s + \mathbf{R}_\nu)$  (see [21]).

In order to find the currents running along the bonds  $s-t$  within the framework of the approximations used above, calculate the quantities  $\mathbf{J}_{st} = \int \mathbf{j}_{st}(\mathbf{r}) d\tau$ . It may be ascertained that

$$\mathbf{J}_{st} = \int \mathbf{j}_{st}(\mathbf{r}) d\tau = 2\alpha c (\alpha Y_{st}^{00} \mathbf{S}_{st} - i Y_{st}^{10}) \mathbf{H}_{st}^{00} (\mathbf{R}_s - \mathbf{R}_t). \quad (13)$$

On the other hand,

$$\mathbf{J}_{st} = \int \mathbf{j}_{st}(\mathbf{r}) d\tau = \int_{\{l\}} dl \int_{\{S_n\}} \mathbf{j}_{st}(\mathbf{r}) dS_n = \int_{\{l\}} dl I_{st}. \quad (14)$$

Here  $\int dl$  and  $\int dS_n$  are a contour and a surface integral, respectively, the element of area  $dS_n$  being always perpendicular to the element of length and  $\mathbf{j}_{st}$  being parallel to  $dl$ . Assuming that the current  $I_{st}$  running between the atoms  $s$  and  $t$  is constant we obtain

$$\mathbf{J}_{st} = \int_{\{l\}} dl I_{st} = I_{st} (\mathbf{R}_s - \mathbf{R}_t). \quad (15)$$

Comparing (13) and (15) we see that the matrix of induced  $\pi$ -electron currents has the following form

$$\mathbf{I} = 2\alpha c (\alpha Y^{00} \circ \mathbf{S} - i Y^{10}) \circ \mathbf{H}^{00}, \quad (16)$$

and the values of diamagnetic susceptibility and chemical shifts (5) and (6) are expressed in terms of the matrix  $\mathbf{I}$  in the following way

$$\chi = -\frac{1}{6c} \text{Sp} (\mathbf{I}\mathbf{S}) \quad (17)$$

$$\begin{aligned} \delta_\nu &= \frac{1}{3c} \text{Sp} [\mathbf{I}(\mathbf{S}_\nu \circ \mathbf{K}_\nu)] + \frac{\hbar^2 \alpha}{m\varepsilon} \text{Sp} (\tilde{\mathbf{Y}}\mathbf{L}_\nu) \\ &\equiv \delta_\nu^{\text{curr}} + \delta_\nu^{\text{loc}}. \end{aligned} \quad (18)$$

The contributions to magnetic shielding are broken down into current ones,  $\delta_\nu^{\text{curr}}$ , and local ones,  $\delta_\nu^{\text{loc}}$ . The latter are associated with the presence of residual  $\pi$ -electron charges on atoms,  $\tilde{Y}_{pq} = Y_{pq} - \delta_{pq}(N_p - 1)$ , where  $N_p$  is the number of  $\pi$ -electrons supplied by the atom  $p$  into the  $\pi$ -system.

Note that the dimensionality of the matrix  $\mathbf{I}$  coincides with that of current. It is easily shown that the first Kirchoff law holds for the matrix elements  $I_{st}$  in the coupled variant of perturbation theory. In fact, consider the first of Eqs. (3) for diagonal elements and take into account the explicit form of matrix  $\mathbf{H}^{10}$  (4), the symmetry of  $\mathbf{Y}^{00}$  and asymmetry of  $\mathbf{Y}^{10}$  and  $\mathbf{S}$ .

We then obtain

$$2\alpha c \sum_s (\alpha Y_{st}^{00} S_{st} - i Y_{st}^{10}) H_{st}^{00} = 0 \quad (19)$$

or, allowing for (16)

$$\sum_s I_{st} = 0, \quad (20)$$

i.e. the sum of the currents running from the node  $t$  is equal to that of the currents toward this node. We emphasize that the formula (20) remains valid if the electron–electron interaction is neglected, which is not the case for the uncoupled variant of perturbation theory (in which the distortion of electron–electron interaction under the influence of the external magnetic field is neglected, i.e.  $G(Y^{10})=0$  in Eq. (3)) whose gauge-noninvariance [23] manifests itself as a violation of the first Kirchhoff law.

Among the consequences of (20) we note the following. In the case when the center  $t$  has only one neighbour (e.g.  $t$  is the last atom in an unclosed chain) only one term remains in the sum (20) which is equal to zero as follows from (20). Thus, the induced current does not run along an unclosed chain of atoms<sup>1</sup>. Specifically, it follows that the  $\pi$ -electron contributions to the chemical shifts and diamagnetic susceptibility are zero. For the latter this was shown already by London, without considering electron–electron interaction [17].

It is noteworthy that for the entities  $J_{st}$  introduced in [34] (analogous to (13)), in the framework of approximations used, the equality

$$\sum_{st} J_{st} = 0 \quad (21)$$

holds exactly. Indeed, since the currents in an unclosed chain are equal to zero expression (21) may be transformed into a sum over irreducible circuits of the molecule

$$\sum_{st} J_{st} = \sum_{st} I_{st} (\mathbf{R}_s - \mathbf{R}_t) = \sum_l I_l \sum_{st \in l} (\mathbf{R}_s - \mathbf{R}_t) = 0 \quad (22)$$

which equals to zero because summation of  $(\mathbf{R}_s - \mathbf{R}_t)$  over any closed contour gives zero. Note also that, since the bond lengths in aromatic molecules are sufficiently close to each other, the entities  $J_{st}$  may be considered approximately proportional to  $\pi$ -electron currents, and they may be used [34] for the description of current distribution in molecules.

In the standard parametrization of the  $\pi$ -electron Hamiltonian, the off-diagonal elements of the matrix  $H^{00}$  are assumed to be different from zero only for the

<sup>1</sup> This does not hold when resonance integrals involving chemically non-bonded atoms are taken into account (see parametrization 2 below) since the molecule is broken down into many circuits the number of which exceeds the number of cycles in the molecular graph.

atoms linked by a  $\pi$ -bond, i.e.

$$H_{pq}^{00} = \begin{cases} \beta_{pq}, & p, q \text{ bonded} \\ 0, & p, q \text{ non-bonded.} \end{cases} \quad (23)$$

In this approximation the number of linear independent elements of the matrix  $I$  proves to be equal to the number of irreducible circuits in a molecule, for example, to the number of benzene rings in polycyclic benzoid compounds. In formulae (17) and (18) the summation over the  $\pi$ -electron centers may be replaced by the summation over these circuits:

$$\chi = -\frac{1}{6c} \sum_l I_l S_l, \quad (24)$$

$$\delta_\nu^{\text{curr}} = \frac{1}{3c} \sum_l I_l K_{l\nu}. \quad (25)$$

Here  $I_l$  is the current in the circuit  $l$ ,  $S_l$  is the area covered by the circuit,  $K_{l\nu} = \sum_{st \in l} (S_\nu)_{st} (K_\nu)_{st}$  is the geometry factor characterizing the  $l$ th circuit.

It should be noted that if in the expression for  $K_{l\nu}$  one takes outside the summation sign the mean distance from the shielded nucleus, then the expression (25) is simplified and takes on the form:

$$\delta_\nu^{\text{curr}} = \frac{1}{3c} \sum_l I_l S_l |\mathbf{R}_{l\nu}|^{-3} \quad (26)$$

which corresponds to the dipole approximation of magnetostatics (see, for example [16]). If in the expression for  $K_{l\nu}$  one proceeds to the limit corresponding to the circuit representation as a circumference [25], then  $K_{l\nu}$  is converted to the sum of two elliptic integrals, while the formula (25) coincides with that obtained by direct calculation of the effective magnetic field created by circular induced currents [13].

Two sets of semiempirical parameters were used in the present work to calculate the magnetic properties of porphyrins. In the parametrization 1 the condition (23) was imposed on the off-diagonal elements of the matrix  $H^{00}$  and there were used the numerical values of the parameters chosen earlier [25–29] from the best agreement of the predicted and experimental proton chemical shifts and the energies of the lowest singlet–singlet transitions of a number of conjugated molecules containing the pyrrole ring. In parametrization 2 [36], the off-diagonal matrix elements  $H_{pq}^{00}$  were assumed to be proportional to the overlap integrals  $\langle p|q \rangle$  and different from zero for all  $p$  and  $q$

$$H_{pq}^{00} = \text{const} \frac{H_{pp}^{00} + H_{qq}^{00}}{1 + \langle p|q \rangle} \langle p|q \rangle. \quad (27)$$

The calculations of spectroscopic properties of porphyrins in parametrization 2 agree with the experiment rather well [37]. The porphin macrocycle geometry was taken from X-ray diffraction data for porphyrins and metallo-porphyrins



[38, 39] and was idealized in such a way that all the C—C and C—N bond lengths were assumed to be equal to 1.4 Å; and the C—H and N—H bond lengths, to 1.0 Å. The use of a real geometry, for example, for porphin and metalloporphin does not cause considerable changes in the results of calculations of the magnetic properties. The presence of a metal atom in the center of the porphin ring was taken into account by averaging the  $\pi$ -electron parameters of the nitrogen atoms in pyridine and pyrrole.

### 3. Results

#### 3.1. Ring Currents

The current distributions (in the units of the benzene ring current) in the molecules under study calculated using the parametrization 1 are given in Figs. 1–5 where the thick lines show the currents along the bridges and the greatest currents in the branched sections of the  $\pi$ -system. It can be seen that the bridge currents of the molecules of interest exceed approximately by a factor of two the benzene ring current. In the pyrrole and benzene cycles of the molecules investigated the current distribution essentially depends on the molecular structure.

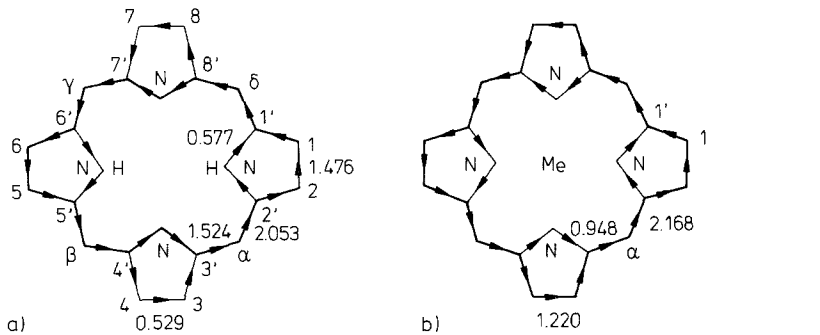


Fig. 1. Current distribution in the molecules of porphin (a) and metalloporphin (b).

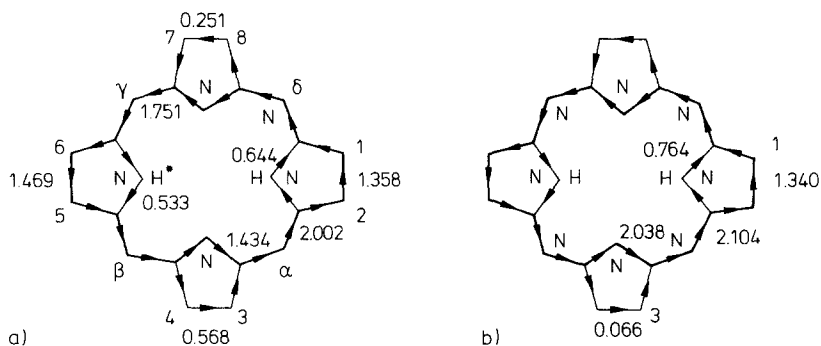


Fig. 2. Current distribution in the molecules of monoazaporphin (a) and tetrazaporphin (b).

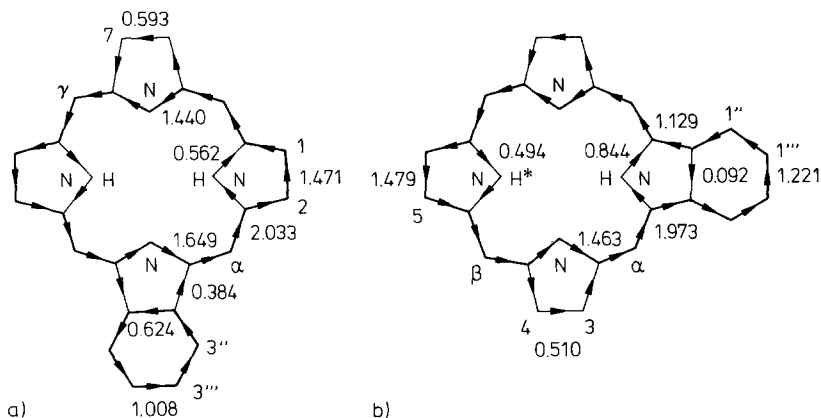


Fig. 3. Current distribution in the molecules of two isomers A and B of monobenzporphin

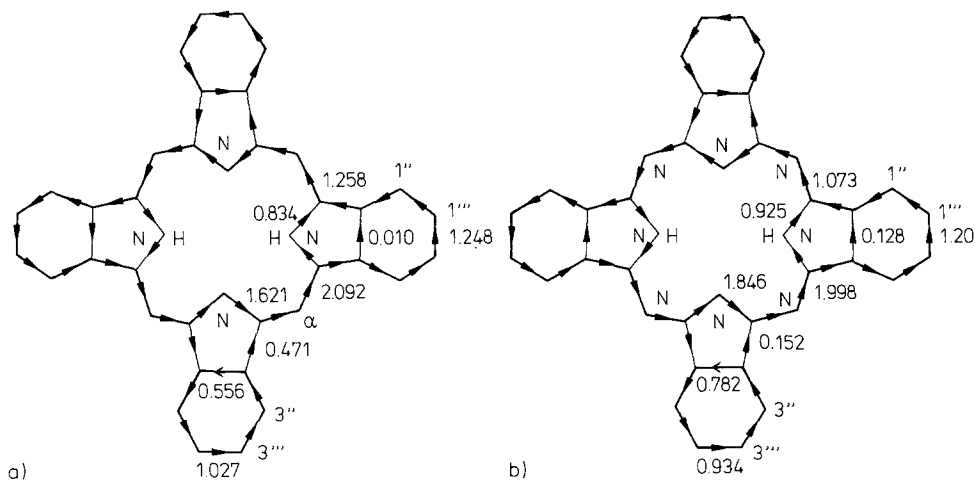


Fig. 4. Current distribution in the molecules of tetrabenzporphin (a) and phthalocyanine (b)

Thus, the methine bridge current of the porphin molecule branches in such a way that the currents along the  $C_3-C_{3'}$ , and  $C_4-C_3$  bonds of the pyrrolenine ring and the  $C_1-N(H)$  bonds of the pyrrole ring amount to only 25% of the methine bridge current. For metalloporphin, the methine bridge current is somewhat higher than for porphin, and branches respectively as 55% and 45% for the external and internal sections of the pyrrole ring chain. Upon the hydrogenation of one pyrrolenine ring (in passing from porphin to chlorin) the methine bridge current falls from 2.053 to 1.884.

For the porphin-phthalocyanine series, it is of interest to follow the effect of aza- and benzo-substitution on the  $\pi$ -electron ring currents. As is seen from Fig. 2a, substitution of one methine bridge by a nitrogen one (monoazaporphin) yields an appreciable redistribution of the currents. This is especially pronounced in the pyrrolenine ring which is the nearest to the nitrogen bridge (e.g. the current along

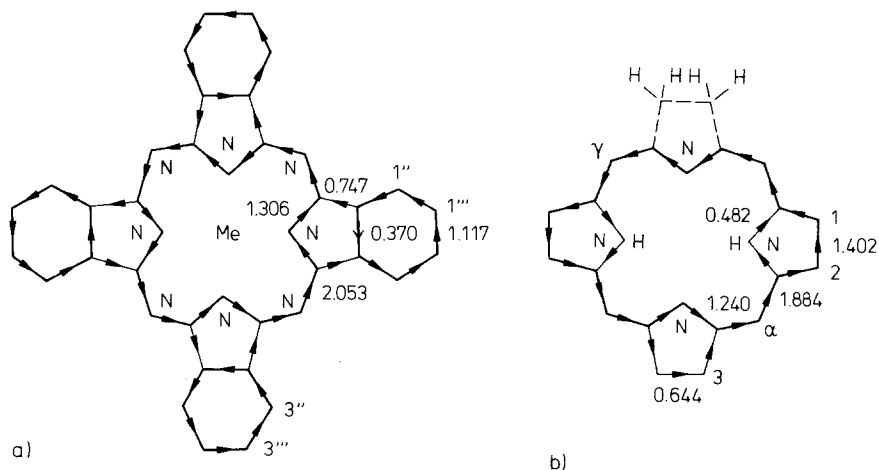
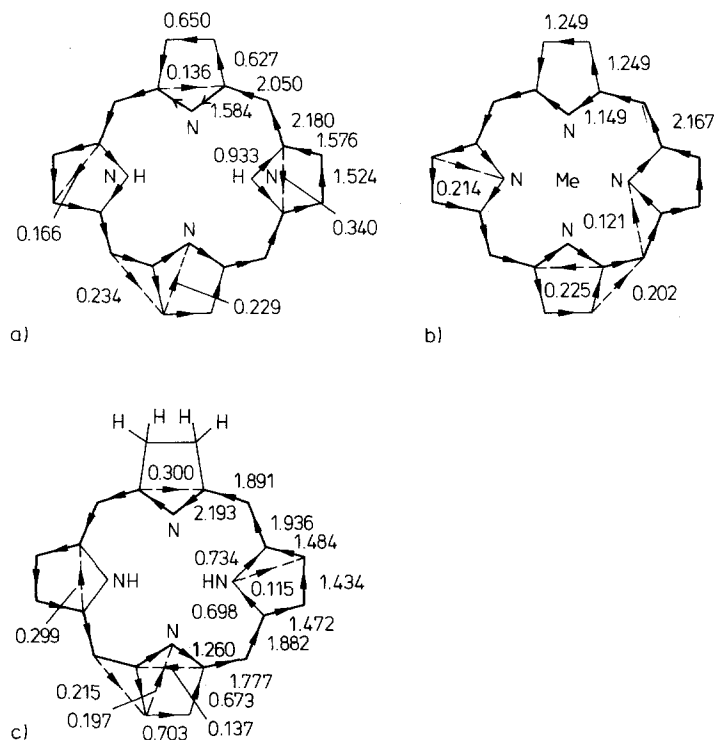


Fig. 5. Current distribution in the molecules of metallophthalocyanine (a) and chlorin (b)

the  $C_7-C_7'$  bond falls from 0.529 to 0.251). For tetrazaporphin (Fig. 2b) the current along the  $C_3-C_3'$  and  $C_4-C_3$  bonds falls practically to zero. The fusion of a benzene ring to a pyrrolenine ring (Fig. 3a, monobenzporphyrin A) exerts a slight influence on the currents in the pyrrole rings and the benzene ring, and causes primarily the current redistribution in pyrrolenine rings. So, the  $C_3-C_3'$  bond current falls from 0.529 to 0.384, whereas the  $C_7-C_7'$  bond current grows from 0.529 to 0.593. The fusion of a benzene ring to a pyrrole ring (Fig. 3b, monobenzporphyrin B) causes some decrease in the methine bridge current, whereas the most pronounced changes are observed in the benzene ring where the current increases by 0.221 as compared to an isolated benzene ring, and in the attached pyrrole ring, where the  $C_1-C_1'$  bond current decreases by 0.347 as compared to porphyrin. It is worth noting that practically no current runs along the  $C_2-C_1$  bond of the monobenzporphyrin B molecule. In general, the current distributions of two monobenzporphyrin isomers indicate more appreciable interaction of the porphyrin macrocycle with the benzene ring in the case of monobenzporphyrin B. The calculated  $\pi$ -electron currents in the tetrabenzporphyrin molecule demonstrate an approximate additivity of the effect of the fusion of benzene rings to pyrrole and pyrrolenine rings on the  $\pi$ -electron currents. Similarly, the analysis of current distributions in the phthalocyanine and metallophthalocyanine molecules (Fig. 4b, 5a) allow a conclusion that aza- and benzo-substitution affect almost in additive manner the  $\pi$ -electron ring currents in the porphyrin-phthalocyanine series. One can say, for example, that tetraza-substitution results in the vanishing of the current along the  $C_3-C_3'$  bonds, while tetrabenzo-substitution, in the vanishing of the current along the  $C_2-C_1$  bonds. In the series of the porphyrin, tetrazaporphyrin, tetrabenzporphyrin and phthalocyanine molecules an increasing "conductivity" of internal sections of pyrrole and pyrrolenine rings is distinctly seen. In fact, for this series the  $C_1-N(H)$  bond current increases to give 0.577, 0.764, 0.834 and 0.925, while the  $N-C_3'$  bond current changes as

1.524, 2.038, 1.621 and 1.846. The current along the N—C bond of metalloporphyrins increases in a similar way from 0.948 for metalloporphyrin to 1.306 for metallophthalocyanine.

Consider in brief the results of calculation of the  $\pi$ -electron currents within the framework of the parametrization 2, in which the condition (23) is not imposed on matrix elements of  $H^{00}$  and, hence, the  $\pi$ -electron currents arise between the atoms not linked by chemical bonds. In Fig. 6, as an example, the distributions of the  $\pi$ -electron currents in the porphin, metalloporphin and chlorin molecules calculated with the set of parameters 2 are represented (the currents greater than 0.1 are given in Fig. 6)<sup>2</sup>. As is seen from these data the use of the parametrization 2 somewhat complicates the current distribution pattern as compared to the parametrization 1, but does not change it qualitatively. Both parametrizations give practically the same results for the magnetic shielding and diamagnetic susceptibility.



**Fig. 6.** Current distribution including currents between non-bonded atoms (parametrization 2) for porphin (a), metalloporphin (b) and chlorin (c)

<sup>2</sup> The benzene ring current values calculated in both parametrizations coincide with the accuracy better than 1%. It should be noted that in parametrization 2 as well as in 1 due to the high symmetry, the elements  $I_{pq} \neq 0$  only for neighbouring atoms of the benzene molecule.

The concept of the main chain of conjugation chosen in form of the 16-, 18- and 20-membered cyclopolyenes is often used when considering physical properties of porphyrins. It must be emphasized, however, that this concept is roughly simplified for branched  $\pi$ -electron systems in which case it is most reasonable to speak of the superposition of conjugation chains. Since the magnetic properties of conjugated systems are determined by the mobility of  $\pi$ -electrons, it is believed that the calculated current distributions make it possible to identify the main conjugation chain and to estimate quantitatively the applicability of this concept. For example, the current distribution of the porphin molecule (Fig. 1a) is such that the currents running along the  $C_3-C_3'$ ,  $C_3-C_4$  and  $C_1-N(H)$  bonds amount only to 25% of the methine bridge current. This enables us to identify the 18-membered ring as a main chain of conjugation. For porphin metal complex the current along the external 20-membered cycle (1.220) is greater than that along the internal 16-membered cycle (0.948). Hence, both cycles are nearly equipollent. However, for a quantitative estimation of the contribution of different cyclopolyenes, the independent currents that may be generated in the pyrrole and pyrrolenine rings must be taken into account. As the result, in the case of metalloporphin, for example, the independent current along the 16-membered ring will increase, while that along the 20-membered ring decrease. This illustrates the general statement on the ambiguity of the choice of the current circuits. At the same time, the above increase in the current along the internal sections of pyrrole and pyrrolenine rings on aza- and benzo-substitution testifies unambiguously the increasing role of the internal 16-membered cyclopolyene in the conjugated system.

### 3.2. Magnetic Shielding

The current and charge contributions to magnetic shielding of protons ( $\delta_\nu^{\text{curr}}$  and  $\delta_\nu^{\text{loc}}$ ) have been obtained from the calculated values of the  $\pi$ -electron charges and the induced  $\pi$ -electron currents. When comparing with the experiment, the effect of the molecular  $\sigma$ -core, steric factors, intramolecular hydrogen bonds, and lone pairs have been considered within the framework of the earlier developed additive scheme [25–28]:

$$\delta_\nu^{\text{calc}} = \Delta_\nu - (\delta_\nu^{\text{curr}} + \delta_\nu^{\text{loc}}) \quad (28)$$

where  $\Delta_\nu = 5.89$  ppm for CH protons and  $\Delta_\nu = 10.79$  ppm for NH protons.

The calculation results on the proton chemical shifts (in parametrization 1) for the molecules investigated are presented and compared with the available experimental data in Table 1. On the whole, as is seen from Table 1, these calculation data are in good agreement with the experiment. Some discrepancies may be presumably explained by the defects of the additive scheme and by the chemical structure peculiarities of the molecules, for example, phthalocyanine (see [40]). It must be noted that the current components  $\delta_\nu^{\text{curr}}$  make a dominant contribution to proton magnetic shielding. The charge component  $\delta_\nu^{\text{loc}}$  does not exceed 5% of the total  $\pi$ -electron contributions, their absolute values being no more than 0.15 ppm for the CH protons and 0.6 ppm for the central NH protons. The latter

**Table 1.** Chemical shifts in  $^1\text{H-NMR}$  of porphyrins (in ppm relative to TMS)

Molecule	Proton	$\delta^{\text{curr}}$	$\delta^{\text{loc}}$	$\delta^{\text{calc}}$	$\delta^{\text{exp}}$	Refs.
Porphin	$\alpha$	-4.79	-0.07	10.75	10.37	[41]
	1	-3.08	0.00	8.97	9.53	
	3	-2.41	0.12	8.18		
	NH	15.22	-0.51	-3.82	-3.94	
Metalloporphin	$\alpha$	-5.20	-0.08	11.16	10.12-10.49	[42]
	1	-3.05	0.05	8.89	9.22-9.52	
Monoazaporphin	$\alpha$	-4.66	-0.12	10.66		
	$\beta$	-4.70	-0.14	10.73		
	$\gamma$	-5.58	-0.08	11.56		
	1	-2.93	0.03	8.79		
	2	-2.94	-0.03	8.86		
	5	-3.02	-0.03	8.94		
	6	-3.01	-0.01	8.91		
	3	-2.38	0.11	8.16		
	4	-2.38	0.10	8.17		
	7	-2.13	0.12	7.90		
	8	-2.13	-0.12	8.14		
	HN	14.82	-0.53	-3.58		
NH*	14.97	-0.51	-3.39			
Tetrazaorphin	1	-2.97	-0.04	8.90		
	3	-2.06	0.06	7.90		
	NH	16.06	-0.53	-4.62		
Monobenzporphin A	$\alpha$	-5.04	-0.01	10.94		
	$\delta$	-4.80	-0.08	10.77		
	1	-3.09	0.00	8.980		
	2	-3.12	0.03	8.981		
	7	-2.45	0.13	8.31		
	NH	14.98	-0.52	-3.57		
	3''	-2.64	0.01	8.52		
	3'''	-1.73	0.02	7.61		
Monobenzporphin B	$\alpha$	-4.91	0.00	10.81		
	$\beta$	-4.65	-0.09	10.63		
	5	-3.02	0.01	8.91		
	3	-2.37	0.14	8.12		
	4	-2.34	0.12	8.11		
	NH	13.18	-0.52	-1.71		
	NH*	13.12	-0.52	-1.71		
	1''	-3.01	-0.05	8.95		
	1'''	-2.02	-0.04	7.85		
Tetrabenzporphin	$\alpha$	-5.57	0.01	11.43	11.29	[42] <sup>a</sup>
	NH	15.20	-0.54	-3.76	—	
	1''	-3.27	-0.03	9.19	9.93	
	3''	-2.84	0.03	8.70		
	1'''	-2.16	-0.02	8.07	8.34	
	3'''	-1.83	0.04	7.68		

**Table 1.** (continued)

Molecule	Proton	$\delta^{\text{curr}}$	$\delta^{\text{loc}}$	$\delta^{\text{calc}}$	$\delta^{\text{exp}}$	Refs.
Phthalocyanine	NH	14.84	-0.58	-3.37	-5.3	[43]
	1''	-3.06	-0.03	8.98	7.5-8.4	
	3''	-2.54	0.03	8.40		
	1'''	-2.03	-0.05	7.98	7.5-8.4	
	3'''	-1.65	0.02	7.51		
Metallophthalocyanine	1''	-2.95	-0.01	8.85	9.17	[42]
					9.60-9.70	[44]
	1'''	-1.94	-0.01	7.83	8.16	[42]
					8.27-8.38	[44]
Chlorin	$\alpha$	-4.46	-0.10	10.45	9.81	[41]
	$\delta$	-4.28	0.07	10.06	8.95	
	1	-2.84	0.06	8.67	8.84	
	2	-2.86	0.00	8.75	9.19	
	3	-2.33	0.15	8.07	9.02	
	NH	14.02	-0.54	-2.59	-2.43	

<sup>a</sup> Data for the zinc complex.

value coincides with the local contribution to the magnetic shielding of the NH proton of the pyrrole molecule [22]. However, the corresponding current contribution for pyrrole is appreciably lower than that of porphyrins and is comparable in its value with the charge contribution. It is seen from Table 1, that the calculated chemical shifts for the NH protons lie at high field ( $\delta_{\nu} \sim -3.5 \div -4.0$  ppm), while for the external protons they are at low field ( $\delta_{\nu} \sim 10 \div 11$  ppm for the bridge protons). These results are in quantitative agreement with the experiment. Moreover, the calculation predicts the chemical shift values for the external protons of pyrrole rings by 1.5-2 ppm lower than those for the protons of methine bridges, which is in agreement with the experiment where the difference observed is about 1 ppm. The changes in chemical shifts on hydrogenation of a pyrrole ring (in passing from porphin to chlorin) are also described well by the theory. For benzo-substituted porphin derivatives the correct values of the chemical shifts of the benzene ring protons are given by the calculations. In general, the results obtained verify unambiguously the assumption of the dominant role of the  $\pi$ -electron ring currents in the magnetic shielding of the protons of the porphyrin molecules made usually in the experimental works [9, 41].

As is noted above, the use of the parametrization 2 does not cause any essential changes in the calculated chemical shifts of the protons of the molecules studied. In fact, the proton chemical shifts calculated using this set of parameters are as follows:  $H_{\alpha} - 10.89$ ,  $H_1 - 9.17$ ,  $H_3 - 8.49$ ,  $NH - (-3.91)$  (porphin);  $H_{\alpha} - 11.31$ ,  $H_1 - 9.15$  (metalloporphin);  $H_{\alpha} - 10.28$ ,  $H_{\delta} - 9.83$ ,  $H_1 - 8.75$ ,  $H_2 - 8.78$ ,  $H_3 - 8.22$ ,  $NH - (-2.12)$  (chlorin).

The charge and current distributions obtained may be used for estimating magnetic shielding of the nuclei different from protons. In this case, a direct use

of formula (18) is incorrect, since if the nucleus being shielded is incorporated in the  $\pi$ -system of the molecule, one of the  $R_{pv}$ 's is zero. In Refs. [27, 28] a linear approximation of the corresponding term was suggested. Then, allowing for the comparative smallness of current contributions to chemical shifts of  $^{13}\text{C}$  and  $^{15}\text{N}$  in heterocyclic systems, magnetic shielding of  $^{13}\text{C}$  and  $^{15}\text{N}$  can be described within a sufficient accuracy by the linear function of the residual  $\pi$ -electron charges on the shielded nuclei

$$\delta_x = A_x \cdot \Delta q_x + B_x \quad (29)$$

where  $A(^{13}\text{C}) = 150$  and  $A(^{15}\text{N}) = 900$ . The coefficient  $B(^{13}\text{C})$  for double-bonded and triple-bonded atoms is 1.1 ppm and 9.1 ppm, respectively, provided the chemical shifts of  $^{13}\text{C}$  are considered relative to benzene;  $B(^{15}\text{N})$  is zero for pyridine-type nitrogen, with pyridine as a reference compound, and it is 630 ppm for pyrrole nitrogen [27, 28]. If the contribution of residual  $\pi$ -electron charges is small, then the current contributions and other terms in formula (18) must be allowed. For the porphin molecule the calculation yields:  $C_1 - 135.1(131.5)$ ,  $C_3 - 136.3(131.5)$ ,  $C_{1'} - 127.5(-)$ ,  $C_{3'} - 128.2(-)$ ,  $C_\alpha - 121.1(104.4)$ ,  $\text{N(H)} - 237(239)$ ,  $\text{N} - 226(132)$ , while for the metalloporphin  $C_1 - 134.7(131.7)$ ,  $C_{1'} - 125.3(149.3)$ ,  $C_\alpha - 120.9(104.3)$ ,  $\text{N} - 192(175)$ . Parenthesized are the experimental data of Refs. [45–47]. Chemical shifts are given in ppm,  $\delta(^{13}\text{C})$  relative to TMS, and  $\delta(^{15}\text{N})$  relative to  $\text{NO}_3^-$ . Note that the experimental values of the  $^{15}\text{N}$  chemical shifts in the porphin and metalloporphin molecules are in fine correlation with the calculated  $\pi$ -electron densities on nitrogen atoms: for porphin  $Y(\text{N(H)}) = 0.665$ ;  $Y(\text{N}) = 0.353$ ; for metalloporphin  $Y(\text{N}) = 0.540$ .

### 3.3. Magnetic Anisotropy

Diamagnetic anisotropy of conjugated molecules is usually considered as one of the qualitative characteristics of aromaticity [24, 48, 49]. Relative  $\pi$ -electron contributions to diamagnetic susceptibility  $\chi' = \chi/\chi$  (benzene) have been determined (see (17)) from the current distributions in the porphyrin molecules and used to construct the aromaticity scale for the molecules studied. In Table 2 the obtained values of  $\chi'$  are presented which increase in the following series:  $\text{X} < \text{IV} < \text{III} < \text{I} < \text{VI} < \text{V} < \text{II} < \text{VIII} < \text{IX} < \text{VII}$ . It is seen from Table 2 that the introduction of a metal atom into the porphin molecule increases its diamagnetic

**Table 2.** Relative  $\pi$ -electron contributions to diamagnetic susceptibility of porphyrins  $\chi' = \chi/\chi$  (benzene),  $\chi(\text{benzene}) = -31.2 \cdot 10^{-6} \text{ cm}^{-3}/\text{mole}$

No.	Molecule	$\chi'$	No.	Molecule	$\chi'$
I	Porphin	13.36	VI	Monobenzporphin B	13.89
II	Metalloporphin	14.53	VII	Tetrabenzporphin	17.69
III	Monoazaporphin	12.85	VIII	Phthalocyanine	16.25
IV	Tetrazaporphin	12.84	IX	Metallophthalocyanine	17.09
V	Monobenzporphin A	14.19	X	Chlorin	12.11



susceptibility, i.e. aromaticity. Monoaza-substitution (III) in the porphin molecule results in a sharp decrease in  $\chi'$ , while the introduction of four nitrogen atoms (IV) is in practice equivalent to the introduction of one nitrogen atom. As might be expected, benzo-substitution increases diamagnetic susceptibility, but just as in other polycyclic conjugated systems this increase is not additive. Thus, the fusion of the benzene and pyrrolenine rings (V) increases  $\chi'$  by 0.83, and not by 1 while the fusion of the benzene and pyrrole rings increases  $\chi'$  only by 0.53. The deviation from 1 of the  $\chi'$  changes on benzene ring addition may serve as a qualitative measure of the interaction between the benzene and porphin rings, and indicates their stronger interaction in the case of monobenzporphin B as compared to isomer A. The introduction of four benzene nuclei results in  $\chi'$  increasing by 4.33. This points to the change in the mode of the interaction of the benzene rings with the porphin macrocycle as compared to monobenzo-substitution.

As is known, the strength of the  $\pi$ -electron currents may also serve as an aromaticity characteristic. The current strength along the bridges (see Figs. 1 through 5) gives another scale of aromaticity

$$X < VI < VIII < III < V < I < IX < VII < IV < II$$

which makes it possible to estimate the aromaticity of the porphin macrocycle. As is seen from the scale obtained the greatest aromaticity of the porphin ring is achieved when it is stabilized by the introduction of a metal atom (II), by tetraza-substitution (IV) and by tetrabenzo-substitution (VII), while monobenzo- (IV, Y) and monoaza-substitution (III) decrease the aromaticity of the porphin macrocycle.

#### 4. Conclusion

The results obtained show that the  $\pi$ -electron ring currents make the major contribution to proton magnetic shielding in the porphyrin molecules. In general, the technique developed allows the chemical shifts of the molecules studied to be described in good agreement with the experiment. Further development of the notion on the relationship between the magnetic properties of porphyrins and their molecular structure will require a wider set of compounds to be studied theoretically and experimentally.

#### References

1. Pauling, L.: J. Chem. Phys. **4**, 673 (1936)
2. Musher, J. I.: J. Chem. Phys. **43**, 4081 (1965); J. Chem. Phys. **46**, 1219 (1967)
3. Dailey, B. P.: J. Chem. Phys. **41**, 2304 (1964)
4. Gaidis, J. M., West, R.: J. Chem. Phys. **46**, 1218 (1967)
5. Jones, A. J.: Rev. Pure Appl. Chem. **18**, 253 (1968)
6. Abraham, R. J., Thomas W. A.: J. Chem. Soc. (London) B, **1966**, 127
7. Blustin, P. H.: Mol. Phys. **36**, 1441 (1978); Mol. Phys. **39**, 565 (1980)

8. Gurinovich, G. P., Sevchenko, A. N., Solovyov, K. N.: Spectroscopy of chlorophyll and related compounds (in Russian) Ch. 3, Minsk: "Nauka i tekhnika" Publishing House 1968
9. Scheer, H., Katz, J. J. in: Porphyrins and Metalloporphyrins, ed. K. M. Smith, p. 399, Amsterdam – New York – Oxford: Elsevier 1975
10. Becker, E. D., Bradley, R. B.: *J. Chem. Phys.* **31**, 1413 (1959)
11. Ellis, J., Jackson, A. H., Kenner, G. W., Lee, J.: *Tetrahedron Letters* **1960**, 23
12. Pople, J. A.: *J. Chem. Phys.* **24**, 1111 (1956)
13. Waugh, J. S., Fessenden, R. W.: *J. Am. Chem. Soc.* **79**, 846 (1957); *J. Am. Chem. Soc.* **80**, 6697 (1958).
14. Johnson, Jr., C. E., Bovey, F. A.: *J. Chem. Phys.* **29**, 1012 (1957).
15. Abraham, R. J.: *Mol. Phys.* **4**, 145 (1961).
16. Pople, J. A., Schneider, W. G., Bernstein, H. J.: High resolution nuclear magnetic resonance. New York: McGraw-Hill Book Co. 1959
17. London, F.: *J. Phys. Radium* **8**, 397 (1937)
18. McWeeny, R.: *Mol. Phys.* **1**, 311 (1958)
19. Pople, J. A.: *Mol. Phys.* **1**, 175 (1958)
20. Mamayev, V. M., Ponomaryov, G. V., Zenin, S. V., Yevstigneyeva, R. P.: *Teor. Eksp. Khim.* **6**, 40 (1970)
21. Vysotsky, Yu. B.: Manuscript deposited with VINITI, September 18, 1975, No. 2671-75; Deponirovannyye Rukopisi No. 9 (59), 68 (1976)
22. Vysotsky, Yu. B.: *Zh. Strukt. Khim.* **19**, 605 (1978)
23. Stevens, R. M., Pitzer, R. M., Lipscomb, W. N.: *J. Chem. Phys.* **38**, 550 (1963); Epstein, S. T.: *J. Chem. Phys.* **42**, 2897 (1965); *J. Chem. Phys.* **58**, 1592 (1973)
24. Roberts, H. G. F.: *Mol. Phys.* **29**, 1277 (1975)
25. Vysotsky, Yu. B.: *Zh. Strukt. Khim.* **13**, 498 (1972)
26. Vysotsky, Yu. B.: *Zh. Strukt. Khim.* **15**, 56 (1974); *Zh. Strukt. Khim.* **15**, 566 (1974); *Zh. Org. Khim.* **14**, 1563 (1978).
27. Vysotsky, Yu. B., Mestechkin, M. M.: *Zh. Strukt. Khim.* **16**, 303 (1975)
28. Vysotsky, Yu. B.: *Zh. Strukt. Khim.* **19**, 736 (1978)
29. Sheinkman, A. K., Mestechkin, M. M., Kucherenko, A. P., Artyomova, V. V., Poltavets, V. N., Vysotsky, Yu. B.: *Khim. Geterotitsikl. Soedin.* **1974**, 537; Sheinkman, A. K., Mestechkin, M. M., Kucherenko, A. P., Klyuyev, N. A., Poltavets, V. N., Maltseva, G. A., Palagushkina, L. A., Vysotsky Yu. B.: *Khim. Geterotitsikl. Soedin.* **1974**, 1096.
30. Hall, G. G., Hardisson, A.: *Proc. Roy. Soc. A*, **268**, 328 (1962)
31. Amos, A. T., Roberts, G. H. F.: *J. Chem. Phys.* **50**, 2375 (1969)
32. McWeeny, R.: *Chem. Phys. Letters* **9**, 324 (1971)
33. Mestechkin, M. M.: *Teor. Eksp. Khim.* **4**, 154 (1968); Mestechkin, M. M.: The density matrix method in the theory of molecules (in Russian), p. 352. Kiev: "Naukova Dumka" Publishing House 1977
34. Coulson, C. A., Gomes, J. A. N. F., Mallion, R. B.: *Mol. Phys.* **30**, 713 (1975)
35. Linderberg, J.: *Chem. Phys. Letters* **1**, 39 (1967)
36. Hammond, H. A.: *Theoret. Chim. Acta (Berl.)* **18**, 239 (1970)
37. Kuzmitsky, V. A., Kravchuk, O. V., Solovyov, K. N.: *Zh. Prikl. Spektrosk.* **33**, 326 (1980)
38. Tulinsky, A.: *Ann. New York Acad. Sci.* **206**, 47 (1973)
39. Collins, D. M., Hoard, J. L.: *J. Amer. Chem. Soc.* **92**, 3761 (1970)
40. Berezin, B. D.: Coordination compounds of porphyrins and phthalocyanine (in Russian), p. 28. Moscow: "Nauka" Publishing House 1978
41. Yegorova, G. D., Solovyov, K. N., Shulga, A. M.: *Teor. Eksp. Khim.* **11**, 77 (1975)
42. Solovyov, K. N., Mashenkov, V. A., Gradyushko, A. T., Turkova, A. Ye., Lezina, V. P.: *Zh. Prikl. Spektrosk.* **13**, 339 (1970)
43. Andronova, N. A., Lukyanets, Ye. A.: *Zh. Prikl. Spektrosk.* **20**, 312 (1974).
44. Janson, T. R., Kane, A. R., Sullivan, J. F., Knox, K., Kenney, M. E.: *J. Am. Chem. Soc.* **91**, 5210 (1969)
45. Abraham, R. J., Pearson, H., Smith, K. M., Loftus, P., Roberts, J. D.: *Tetrahedron Letters* **1976**, 877

46. Yeh, H. J. C., Sato, M., Morishima, I.: *J. Magn. Resonance* **26**, 365 (1977)
47. Gust, D., Roberts, J. D.: *J. Am. Chem. Soc.* **99**, 3637 (1977)
48. Lazzeretti, P., Taddei, F.: *Mol. Phys.* **22**, 941 (1971)
49. Cook, M. J., Katritzky, A. B., Linda, P.: *Adv. Heterocyclic Chem.* **17**, 255 (1974)

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