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SOME PECULIARITIES OF THE MOLECULAR STRUCTURE OF PORPHINE AND ITS COMPLEXES

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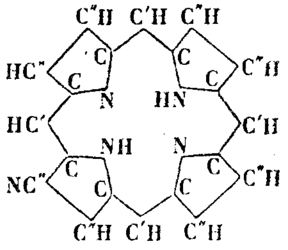
A qualitative analysis of certain peculiarities of the porphine molecule and its complexes compared with the phthalocyanine molecule is made by evaluating the π-electron charges of bonds in these compounds by means of G. V. Bykov's semi-empirical linear equation. Acid-base, oxidation-reduction, and coordination properties of porphine are examined. It is shown that differences in chemical properties of porphines and tetraporphines can be explained by differences in π-electron charges of bonds.

Recently there has been great interest in the structures of the porphine molecule, its numerous derivatives (porphyrins) and their complex salts, as some of these compounds are biologically active. Porphine and its derivatives form the subject of numerous experimental [1-4] and theoretical investigations [5-15]. However, difficulties in interpreting many properties of porphines two decades ago [12] still exist. They arise not only when considering the altogether complex optical properties of porphines [13-15], but also when analyzing chemical properties [12]. Actually, as far as is known, up to the present the literature has not contained any consideration of the question of what causes differences between properties of molecules with porphine and tetrazaporphine rings, e.g., the greater capacity for coordination possessed by tetrazaporphine and phthalocyanine (i.e., the greater stabilities of their complexes) in comparison with porphines. The reasons for the decrease in thermal stability of porphines and their increased stabilities towards oxidizing agents as compared with tetrazaporphines and phthalocyanines, were not considered. The causes of the much greater basic properties of porphines in comparison with porphyrazines remain unexplained. The basic differences regarding methylation of the imino hydrogens of porphines and phthalocyanines, and a number of other problems, have not been considered.

Some structural peculiarities of the porphine molecule I and of its derivatives can be examined on a basis of evaluation of π-electron charges of bonds. This approach, which has been realized by the present author in the case of the phthalocyanine molecule [16], has made it possible to understand some peculiarities of their chemical properties.



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Approximate calculations of π-electron charges of porphine bonds ($A_{X-Y}\pi$) have been made using G. V. Bykov's semi-empirical linear equation [17], which for C–C and C–N porphine bonds has the forms:

$$L_{C-C}=1.54-0.149\,A_{C-C}^{\pi}\ ; \qquad (1)$$

$$L_{C-N}=1.47-0.094\,A_{C-N}^{\pi}. \qquad (2)$$

There L is the length of the conjugated bonds; 1.54 and 1.47 are the standard lengths of the C–C and C–N bonds in nonconjugated molecules, where the π-electron charge of bonds is zero; 0.149 and 0.094 are specific contractions of the C–C and C–N bonds respectively, when the π-electron charge is unity. The most reliable lengths for the C–C and C–N bonds in porphine were found by X-ray analysis, and are given in a paper by Kobayashi [10]. According to his data, the lengths of the C″–C″, C″–C, C–C′, and C–N bonds are, respectively, 1.37, 1.43, 1.41, and 1.38 Å. The π electron charges of the bonds found by equations (1) and (2) are

$$A_{C''-C''}^{\pi}=1.15,\ A_{C''-C}^{\pi}=0.74,\ A_{C'-C}^{\pi}=0.87,\ A_{C-N}^{\pi}=0.96.$$

It appears that the π-electron charge of the C″–C″ bond is intermediate between that in benzene (0.93) and in ethylene (1.40). It is somewhat greater than the (corresponding) value for C″–C bonds (0.74), indicating a more powerful π electron interaction of the atoms of C″–C″, and a weaker one for the atoms in C″–C. However the π-electron interaction for C"−C in porphine is considerably greater, as A^{π} shows, than in the C−C' bonds of phthalocyanine, with benzene rings in the macro-ring ($A_{C-C}\pi = 0.33$ [16]). This leads to decrease in π-electron interaction in C−C' and C−N bonds, and to a more powerful disturbing action by HC"−C"H side groups of the porphine at the macromolecule as compared with the action of the benzene rings in phthalocyanine. Calculation as well as the chemical and physicochemical properties of phthalocyanine [16] show that its macro-ring and benzene rings are chromophores which are actually almost independent of one another. This cannot be said of the macro-ring and HC"−C"H groups in porphine. It is this that gives rise to the more complex spectrum picture for the porphines.

The comparatively high π-electron density of the C"−C bonds in porphine (compared with C−C' in phthalocyanine) and the presence of a total of only four nitrogen atoms (porphyrazine and phthalocyanine each have 8) leads to a real decrease in $A_{C-N}\pi$ in the macro-ring (0.96), in comparison with phthalocyanine (1.38), to non-equivalence of π-electron charges of the C−N and C−C' bonds, and to increase in radius of the porphine "aperture."

The low π electron charge of the bonds of the macromolecule of the porphines gives rise to real differences in chemical properties in comparison with phthalocyanine, to lower aromaticity, and to lower thermal and chemical stabilities [18]. An obvious consequence of the lower aromaticity of the porphines is their lessened electron affinity, which shows itself primarily in diminished capacity to form dative π-bonds with cations, which are carriers of d-electrons with t_{2g} symmetry. This leads to diminished stability of porphine complexes (with Cu^{2+}, Ni^{2+}, Pd^{2+}, Co^{2+}) as compared with the phthalocyanine ones, and is confirmed by the applicability of spectral criteria of stability to porphine complexes. This criterion is inapplicable strictly to phthalocyanine complexes with powerful dative π-bonds [19].

Evidently the low π-electron charge of bonds of the macro-ring of porphines is a main cause of the stability of their macro-ring towards oxidizing agents. The continuous increase in capacity to resist oxidation, observed when one, two, three, and four methine groups are introduced in succession into the macro-ring of phthalocyanine, is accompanied, it must be assumed, by a gradual decrease in bond π-electron charge. Minimum susceptibility to oxidation and hydrolytic splitting of the macro-ring in acid medium is found precisely with the porphyrins. In acid medium phthalocyanine very readily oxidizes, and also undergoes hydrolytic splitting with opening of the macro-ring [21].

The high "aperture" dimension of porphines as compared with tetrazaporphine and phthalocyanine makes possible formation of rather stable covalent complexes of the intra-orbital sp^2d type with the large cations Cd^{2+}, Hg^{2+}, etc. This latter is not characteristic of phthalocyanines. In its turn the increased "aperture" is apparently one of the causes of the diminished strengths of σ bonds compared with phthalocyanine, which leads to an increase in their capacities to dissociate in acid medium (e. g., complexes with Zn^{2+}).

One of the important peculiarities of the porphine molecule is the high degree of participation in conjugation of non-covalent electron pairs of the nitrogen atoms. The degree of participation of these pairs in conjugation with π electrons of the macro-ring of phthalocyanine is very great, amounting, according to approximate calculations, to more than 50%, and results in π-electron charges of C−N in it, somewhat exceeding unity (1.38). On the other hand in porphine $A_{C-N}\pi$ and $A_{C-C'}\pi$ are less than unity. From these facts it can be concluded that the electron pairs in porphines have primarily σ character. The degree of participation of these pairs in conjugation can be approximately evaluated from the π-electron charges of the porphine bonds. Assuming the π-electron charges of the C−H bonds in porphine to be close to zero (less than 0.08), and considering that the electron pairs of the hetero atoms in porphine participate primarily in the formation of π-electron charges of C−N bonds, and to an altogether small extent in C−C' bonds, it is possible to evaluate the number of electrons of noncovalent pairs of N atoms participating in conjugation. It is equal to $8(A_{C-N}\pi - A_{C-C'}\pi) \approx 0.8$, i.e., only one of the 8 electrons of the noncovalent pairs of the hetero atoms participates in conjugation. Hence the degree of participation of these pairs in conjugation is about 10%. The analogous value for phthalocyanine is over 50% [16]. The evaluation for porphine is quite approximate, as it is carried out with the assumption that interaction of electron pairs is confined to C atoms, and is negligibly small with C'− and C"− atoms. Still, the figures given make it possible to postulate a much more profound capacity for protonization for porphine than for phthalocyanine. This conclusion is in agreement with what is found experimentally: porphines readily undergo two-fold protonization even in dilute acids [2], while phthalocyanine is singly protonized even in 70-100% H_2SO_4, even though it contains twice as many hetero atoms. It is very interesting that porphines [20] are much weaker acids than phthalocyanines. Apparently this is due to the lower degree of participation of electron pairs of atoms of nitrogen of the porphines in conjugation. So favorable energy conditions for internal ionization of the imino hydrogen atoms do not arise, and they remain localized at the nitrogen atoms in the form of NH. Their localization is confirmed by experiments [22] on methylating porphine imino groups. In its turn the high degree of participation of electron pairs of hetero atoms of phthalocyanine in conjugation can be a sufficient reason for delocalization of two of its "imino hydrogen" atoms through internal ionization. Such ionization leads to freeing of two electron pairs, which enter into intense conjugation with π-electrons of the macro-ring of the phthalocyanine.

The identical behaviors of the electronic absorption spectra of phthalocyanine and its stable complexes on protonation ($H_2Pc \rightarrow H_2PcH^+$ and $MPc \rightarrow MPcH^+$) in sulfuric acid leads to the conclusion that protonation of phthalocyanine (H_2Pc) takes place at the periphery of the molecule, and not at the center, as it does with porphines. This is one of the facts which supports experimentally the possibility of internal ionization of H_2Pc, making protonation of the molecule at the center energetically less advantageous, and giving rise to more acidic properties of phthalocyanine as compared with porphyrins.

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