INFLUENCE OF ELECTRONEGATIVE SUBSTITUENTS ON THE ELECTRONIC SPECTRA OF THE PORPHYRINS IN THE FORM OF DICATIONS

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The positions of the electronic absorption bands and also the intensities of the Soret bands of the porphyrins with ethoxycarbonyl substituents in the form of dications have been calculated by the LCAO MO method in Hückel's approximation. Comparison with the experimental results shows good agreement.

In a preceding communication [1] it was shown that in the case of the porphyrins with ethoxycarbonyl substituents there is a linear relationship between the energies of the π–π^* transitions calculated in Hückel's approximation and the experimental data for the Soret bands and the long-wave bands of the absorption in the visible region. The applicability of the theory to the qualitative prediction of the intensity of the Soret bands was also shown.

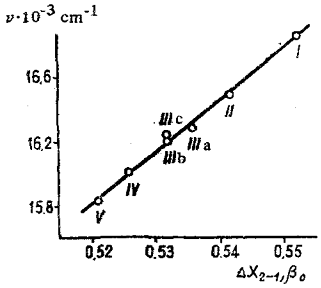

Fig. 1. Correlation between experimental values of the wave numbers of the maxima of the long-wave absorption bands in the visible region and the calculated transition energies $\Delta x_{2,1} = E_1 - E_2$ for compounds I–V in the form of dications.

When the porphyrins pass into the form of dications, there is an increase in the symmetry of the conjugated porphin system, which causes a degeneracy of the pair of excited states that are responsible for the appearance of absorption bands in the visible region and of another pair of excited states responsible for the appearance of the Soret band. As a result of this, the four-band spectrum in the visible region becomes a two-band spectrum, and the Soret band becomes narrower and shifts to longer wavelengths [2].

In the present paper, the energies of the π–π^* transitions obtained by the simple Hückel method are compared with the experimental values of the wave numbers of the maxima of the Soret band and the long-wave absorption bands in the visible region, and the experimental molar extinction coefficients of the Soret bands are compared with the corresponding calculated squares of the dipole forces of the transitions for the same porphyrins in the form of dications: 1,4,5,8-tetramethylporphin (**I**), 2-ethoxycarbonyl-1,4,5,8-tetramethylporphin (**II**), 2,3-diethoxycarbonyl-1,4,5,8-tetramethylporphin (**IIIa**), 2,6-diethoxycarbonyl-1,4,5,8-tetramethylporphin (**IIIb**), 2,7-diethoxycarbonyl-1,4,5,8-tetramethylporphin (**IIIc**), 2,3,6-triethoxycarbonyl-1,4,5,8-tetramethylporphin (**IV**), and 2,3,6,7-tetraethoxycarbonyl-1,4,5,8-tetramethylporphin (**V**).

To perform the calculation we used the set of empirical parameters compiled by B. and A. Pullman [3]. The Coulomb integral is the same for all the nitrogen atoms and is equal to $\alpha_0 + 1.5\,\beta_0$, where α_0 and β_0 are the Coulomb and resonance integrals for the carbon atom. The spatial interaction of the adjacent ethoxycarbonyl groups [4] was taken into account by a reduction in the resonance integral for the bond connecting the ethoxycarbonyl group with the aromatic ring from β_0 to $0.9\,\beta_0$. The dipole forces of the transitions were evaluated from the formula [5].

$$R_y(a, b) = \sqrt{2} \sum_{k=1}^{n} c_{ak} c_{bk} y_k,$$

where c_{ak} and c_{bk} are the coefficients of the molecular orbitals a and b between which the transition takes place, and y_k is the y-coordinate of the k-th atom. To calculate the dipole forces, the geometry of porphin given by Welb and Fleischer [6] was used. The diagonalization of the matrices was carried out by Jacobi's method on an Elliott-803 computer.

Table 1

Energies of the Molecular Orbitals for Porphyrins with Ethoxycarbonyl Substituents in the Form of Dications

Orbitals	I	II	IIIa	IIIb	IIIc	IV	V
Free							
1	−0.131	−0.112	−0.100	−0.093	−0.093	−0.082	−0.071
Occupied							
2	0.422	0.430	0.436	0.439	0.439	0.444	0.450
3	0.632	0.633	0.633	0.633	0.633	0.633	0.633

Table 2

Experimental Molar Extinction Coefficients ε and Calculated Squares of the Dipole Forces R^2 for Porphyrins with Ethoxycarbonyl Substituents in the Form of Dications

Indices	I	II	IIIa	IIIb	IIIc	IV	V
$\varepsilon \cdot 10^{-5}$	1.97	2.22	2.50	2.65	2.72	2.78	3.10
R^2, $(\text{Å})^2$	4.594	4.710	4.768	4.847	4.841	4.926	5.014

To obtain the porphyrins in the form of dications, their solutions in chloroform were saturated with gaseous hydrogen chloride. When the concentration of hydrogen chloride was changed, it was possible to observe isobestic points, which showed the presence of only two types of absorbing molecules. The concentration of the porphyrins in the solutions was about 10^{-4} M for studying the absorption bands in the visible region and 10^{-6} M for the Soret bands. The measurements were carried out in SF-2M and SF-4 spectrophotometers. The errors of measurement of the wavelength were of the order of ±1 nm and those of the molar extinction coefficients, ε, ±10%.

DISCUSSION OF THE RESULTS

In the spectra of the dications, as in the spectra of the free bases [1], the long-wave absorption band in the visible region is assigned to a one-electron transition between the highest occupied and the lowest free molecular orbital, and the Soret band to the transition between the next occupied and the same free molecular orbital. The values of x_i for the molecular orbitals, determined from the energies $E_i = \alpha_0 + \beta_0 x_i$ are given in Table 1.

A comparison of the experimental and calculated transition energies is shown in Figs. 1 and 2.

It can be seen that for all the compounds with the exception of the isomeric diethoxycarbonyltetramethylporphyrins, there is a linear relationship between the calculated and experimental transition energies within the limits of experimental error. The deviation may be explained not only by the defects of the simple Hückel theory, the neglect of singlet-triplet splitting and configurational interaction, but also by the fact that the calculations were carried out on the assumption of isolated molecules. Because of this, the use of experimental data on the absorption spectra of the porphyrins in solutions leads to a disturbance of linearity where the effects of interaction with the solvent are different for the different substances. The existence of such differences is indicated by the fact that with an increase in the concentration of porphyrins in the solutions to 4×10^{-6} M there is a considerable shift of the Soret band (of 1 nm) in the direction of greater wavelengths for compounds I, **IIIa**, **IIIb**, and **IIIc** and in the direction of shorter wavelengths for compound **IV**. Compounds **II** and **V** show no appreciable displacement. We may note that shifts of the order of 1nm can be detected since the accuracy of the determination of the wavelengths with respect to any peak taken as standard is greater than 1 nm.

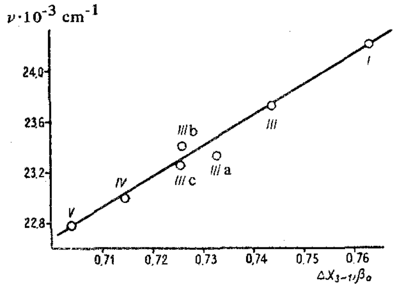

Fig. 2. Correlation between the experimental values of the wave numbers of the maxima of the Soret bands and the calculated transition energies $\Delta x_{3,1} = E_1 - E_3$ for compounds I–V in the form of dications.

A comparison of the experimental molar extinction coefficients ε for the Soret bands with the calculated squares of the dipole forces R_2 (approximately we can take $R^2 \sim \varepsilon$) [7], shows that in the case of the dications, as in the case of the free bases, the Hückel approximation can be used for quantitative predictions.

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