# THE EFFECT OF ELECTRONEGATIVE SUBSTITUENTS ON THE ELECTRONIC SPECTRA OF PORPHYRINS

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The Hückel approximation MO method is used to calculate $\pi$-electron levels of energy and forces of dipole transitions, giving rise to a Soret absorption band in the spectra of porphyrins with carbethoxyl substituents. Comparison with experimental data shows that the theory correctly represents changes in electronic absorption spectra with changes in structure.

A large number of theoretical and practical papers are concerned with the physicochemical properties of porphyrins. The interest of the researcher in this class of compounds is due to peculiarities in their structures, connected with the presence of a macrocyclic conjugated system, the possibility of a high degree of symmetry, and their important role in biochemical processes.

Changes in structures of porphyrins are usually rather clearly manifest in their electronic spectra, which have four weak bands in the visible region, which Stern [1] labels, starting with the longwave one, I, II, III, IV, as well as a very strong Soret band at the limit between the visible and UV regions. Bands I and III belong to separate electron transitions, and II and IV to electron-vibration transitions. The Soret band is due to two electron transitions of almost equal energy.

Both electronic transitions giving rise to bands in the visible region are unlikely, while the transitions connected with the Soret band are permitted [2]. Introduction of substituents into the porphyrin ring has a disturbing effect, mixing electron levels and partly lifting the exclusion. The most marked changes in spectrum are observed when electronegative substituents are introduced.

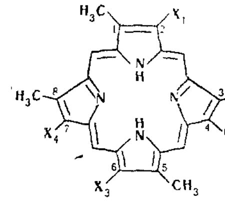
The present paper compares the theoretically calculated electronic spectra with the experimental results for a number of porphyrins with a successively increasing number of electronegative substitutents. The Hückel approximation of the LCAO MO method was used to make the calculations. This method was chosen because of its great practicability compared with the more complete methods, involving considerable computing difficulties, of Pople [3] and Pariser and Parr [4]. The Hückel method previously gave [5–7] satisfactory results for other porphyrins.

Table 1

Squares of Transition Moments and Molar Extinction Coefficients for the Soret Bands

| | Compound | | | | | | |
|---|---|---|---|---|---|---|---|
| | I | II | IIIa | IIIb | IIIc | IV | V |
| $R^2$, $(Å)^2$ | 4.278 | 4.413 | 4.499 | 4.571 | 4.560 | 4.653 | 4.749 |
| $\varepsilon \cdot 10^{-5}$ | 1 48 | 1.62 | 1.75 | 2.11 | 1.93 | 2.13 | 2.40 |

$\pi$-electron energy levels and dipole transition forces leading on the 4-orbital model [7–9] to the appearance of Soret bands, are calculated for the following porphyrins: 1,4,5,8-tetramethylporphyrin (I), 1,4,5,8-tetramethyl-2-carbethoxyporphyrin (II), 1,4,5,8-tetramethyl-2,3-dicarbethoxyporphyrin (IIIa), 1,4,5,8-tetramethyl-2,6-dicarbethoxyporphyrin (IIIb), 1,4,5,8-tetramethyl-2,7-dicarbethoxyporphyrin (IIIc), 1,4,5,8-tetramethyl-2,3,6-tricarbethoxyporphyrin (IV), and 1,4,5,8-tetramethyl-2,3,6,7-tetracarbethoxyporphyrin (V).



I, $X_1=X_2=X_3=X_4=H$
II, $X_1=CO_2C_2H_5$; $X_2=X_3=X_4=H$
IIIa. $X_1=X_2=CO_2C_2H_5$; $X_3=X_4=H$
IIIb, $X_1=X_3=CO_2C_2H_5$; $X_2=X_4=H$
IIIc, $X_1=X_4=CO_2C_2H_5$; $X_2=X_3=H$
IV, $X_1=X_2=X_3=CO_2C_2H_5$; $X_4=H$
V, $X_1=X_2=X_3=X_4=CO_2C_2H_5$

## EXPERIMENTAL

The porphyrins were prepared as previously described [10]. In addition compound IIIb was isolated in insignificant yield. TLC was used to separate and purify the porphyrins.

In investigating visible region absorption bands, the absorption spectra were observed in $CHCl_3$ at concentrations of $10^{-4}$–$10^{-5}$ M with a SF-10 spectrophotometer. To get the outlines of the Soret bands, the concentration of the substance was lowered to $10^{-6}$ –$10^{-7}$ M, and a SF-4 spectrophotometer used. The absorption spectrum of each compound was observed at 3 different concentrations, ratios 1:2:4. The

Table 2

Values of $x_i$

| Orbitals | $x_i$ for compound | | | | | | |
|---|---|---|---|---|---|---|---|
| | I | II | IIIa | IIIb | IIIc | IV | V |
| Free | | | | | | | |
| 1 | −0.331 | −0.330 | −0.329 | −0.329 | −0.329 | −0.328 | −0.328 |
| 2 | −0.244 | −0.227 | −0.217 | −0.212 | −0.212 | −0.203 | −0.193 |
| Occupied | | | | | | | |
| 3 | 0.297 | 0.301 | 0.302 | 0.303 | 0.303 | 0.305 | 0.307 |
| 4 | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 | 0.548 |

extinction coefficients ε given in Table 1 are the means of the three sets of values. The error in determining ε was estimated to be ±10%, and the error in determining the wavelength as ±1 nm.

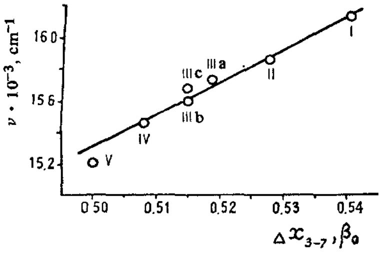


Fig. 1 Correlation between experimentally found wave numbers of maxima of long-wave absorption bands, and calculated energies of $\Delta x_{3-2}$ transitions for compounds I–V.

**Method of calculation.** In the LCAO MO method, the molecular orbitals are represented by

$$\psi_i = \sum_{k=1}^{n} c_{ik}\varphi_k,$$

and their energies by $E_i = \alpha_0 + x_i\beta_0$, where $\alpha_0$ and $\beta_0$ are respectively the Coulomb and resonance integrals for a carbon atom. The values of $c_{ik}$ and $E_i$ are found by solving a system of linear homogeneous equations $\sum_{k=1}^{n} c_{ik}(H_{lk} - E_i S_{lk}) = 0$. In the Huckel approximation $S_{lk} = \delta_{lk}$; $H_{lk} = 0$, and for nonadjacent atoms $H_{kk} = \alpha$; $H_{lk} = \beta$. The choice of empirical parameters set up by Pulman and Pullman [11] was used. All 4 nitrogen atoms were assumed equivalent, and their Coulomb integral taken as $\alpha + 0.7\beta$. The C—N bond resonance integral was taken as $0.95\beta$, and the resonance integral for the C—C bond joining the carbethoxy group to the aromatic ring as $0.95\beta$ when there is steric interaction between carbethoxy groups (compounds IIa, IV, V), and as $\beta$ when there is no steric interaction. For the methyl group a heteroatom model is assumed with Coulomb integral $\alpha_0 + 2\beta$ and resonance integral $0.7\beta$.

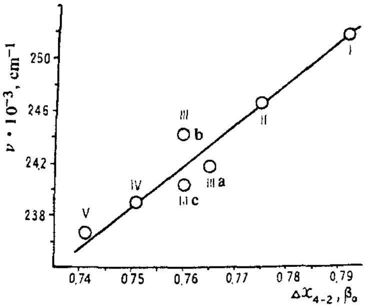


Fig. 2 Correlation between experimentally found values of wave numbers for maxima of Soret bands and calculated transition energies $\Delta x_{4-2}$ for compounds I–V.

The dipole forces were found by means of the formula

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

(in the simple LCAO MO method radiation is absorbed by transition of an electron from a full orbital *a* to a vacant one b). $c_{ak}$ and $c_{bk}$ are molecular orbital coefficients, and a, b, $y_k$ are the coordinates of the k-th atom. The geometry of a porphyrin, given in [13], was used in calculating dipole transition forces.

An Elliott 803 electronic computer was used to carry out the calculations.

**Transition energies.** According to the 4-orbital model, the Soret band and the bands in the visible region of the spectrum arise through transitions between two upper occupied and two lower free orbitals. Table 2 gives results of calculating $x_i$ entering the expression for the energies of those molecular orbitals.

The frequency for the transition between orbitals a and b is given by the expression $h\nu_{ab} = E_b - E_a = (x_a - x_b) \cdot \beta = \Delta x_{ab}\beta$. When using the wave number $\nu$ instead of the frequency $\tilde{\nu}$, $\nu_{ab} = \beta\,\Delta x_{ab}/hc$. Thus if the theory predicts the relative values of the transition energies correctly, there should be a linear relationship between the experimentally found wave numbers $\nu_{ab}$ and the corresponding transition energies $\Delta x_{ab}$.

Table 3
Squares of Forces of Dipole Interactions, in (Å)$^2$

| Transition | $R^2$ for compound | |
|---|---|---|
| | I | V |
| 3—2 | 6.297 | 6.516 |
| 3—1 | 5.644 | 5.056 |
| 4—2 | 4.278 | 4.749 |
| 4—1 | 4.283 | 4.310 |

Figures 1 and 2 show that the simple LCAO MO theory represents the relative changes in transition energies quite satisfactorily. It must be remembered that the calculated transition energies would have to be compared with the experimental data for vapors of porphyrins, since absorption bands are displaced because of solvent-solute interaction or aggregation of the molecules. For example, comparison of the absorption spectrum of the vapor of meso-tetraphenylbenzporphine with that of its benzene solution [14] shows that the Soret band is shifted by 780 cm$^{-1}$. The visible region absorption bands are displaced much less. In the present case the maximum deviation from linear dependence is found for Soret bands in the spectra of dicarbethoxy-substituted porphyrins IIIa, and IIIc. Obviously this is connected with differences in their interactions with the solvent.

**Intensities.** Simple LCAO MO theory cannot explain many regularities in the intensities of the electronic absorption bands of porphyrins. For example, Table 3 gives, for compounds I and V, dipole interaction forces (4–1, 4–2) corresponding to the Soret band, and (3–1, 3–2) to absorption bands in the visible region, which are almost equal when calculated inside the framework of the theory, while in reality the intensity of the Soret band is almost $10^2$ times greater.

The basic difficulties in interpreting the absorption spectra of porphyrins could be solved by calculating the configurational interaction [7–9, 15]. Gouterman [7] using the symmetry perturbation method [16] and the theory of second order perturbation, successfully considered the effect of substitution on the intensities of I and III absorption bands. It was considered that in the absence of perturbation, transition leading to their appearance are forbidden. In the presence of perturbation whose elements were determined from experimental data, the prohibition is partially lifted.

Obviously, in general, any treatment of band intensities inside the framework of the Hückel approximation only is impossible.

With a view to checking whether the Hückel theory could predict the change in intensities of the Soret bands, even if only purely qualitatively, the dipole forces were calculated for the appropriate transitions and compared with the experimental values. The square of the force of dipole interaction is connected with the molar extinction coefficient of a given band by the relationship [17] $R^2 \simeq \text{const} \cdot \varepsilon \cdot \Delta\nu/\nu_0$, where $\Delta\nu$ is the half-width of the band, and $\nu_0$ is the wave number of its maximum. Regarding the change in the ratio $\Delta\nu/\nu_0$ as negligible compared with the relative error in determining the molar extinction coefficient $\varepsilon$, we have

$$R' \simeq \text{const} \cdot \varepsilon.$$

Table 1 compares the experimental values of $\varepsilon$ with the calculated value of $R^2$. It can be seen that the change in the squares of the forces of the dipole interactions correspond qualitatively to the experimental results.

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