To construct the pH/R_f diagrams the arithmetic mean values of the R_f from 5 repeated experiments were used. The mean error was ±0.03 of the R_f values.

In the study of the dependence of the R_f values on the temperature, the chromatographic chamber was placed in a thermostatted vessel.

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INFLUENCE OF π-ELECTRONIC CHARGES ON THE CHEMICAL SHIFTS OF THE meso-PROTONS IN β-ETHOXYCARBONYL-SUBSTITUTED PORPHYRINS

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A calculation has been made of the influence of the electric field of π-electronic charges on the chemical shifts of the meso-protons in β-ethoxycarbonyl-substituted porphyrins. A comparison of the calculated and experimental figures shows that the change in the chemical shifts taking place with the introduction of ethoxycarbonyl substituents into the β-position is due mainly to the changes in the π-electronic charges.

It is known that the presence of an electric field effects the screening constant of an atom [1]. The source of the electric field acting on an atom in a molecule is the charges on the individual atoms. In conjugated molecules, considerable changes in the distribution of charges take place when electro-negative substituents of the type of formyl and ethoxycarbonyl groups and groups similar to them are introduced [2]. These changes appear fairly clearly in the proton resonance spectra [3].

We have considered the influence of the electric fields of the π-electronic charges on the chemical shifts of the meso-protons in β-ethoxycarbonyl-substituted porphyrins: 2-ethoxycarbonyl-1, 4, 5, 8-tetramethylporphin (**II**), 2, 3-diethoxycarbonyl-1, 4, 5, 8-tetramethylporphin (**IIIa**), 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) in the form of dications.

The spectra of 0.03 M solutions of these compounds in deuteriochloroform with the addition of deuteriotrifluoroacetic acid were recorded on a JNM-C-60 spectrometer at 25° C. Hexamethyldisiloxane was used as internal standard.

In order to isolate the effects of the ethoxycarbonyl substituents, the calculation of the chemical shifts was made from the signals of the meso-protons of 1, 4, 5, 8-tetramethylporphin (I) ($\tau \simeq -90$ ppm).

The distribution of the π-electronic charges for compounds **I–V** in the form of dications calculated by

Contributions of the π-Electronic Charges ($\Delta\tau_q$) and Ring Currents of the π-Electrons ($\Delta\tau_k$) to the Chemical Shifts of the meso-Protons relative to 1, 4, 5, 8-Tetramethylporphin.

Compound	$\Delta\tau_q$, ppm	$\Delta\tau_k$, ppm	$\Delta\tau_q+\Delta\tau_k$	Experiment
II	0.66	−0.05	0.61	0.78
IIIa	1.34	−0.06	1.28	1.74
IIIв	0.82	−0.06	0.76	0.71
IV	0.70*	−0.09	0.61	0.70
	1.60**	−0.10	1.50	1.60
V	1.60	−0.11	1.49	1.60

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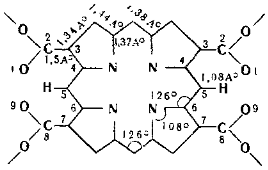
*For a meso-proton adjacent to one ethoxycarbonyl group.

**For a meso-proton located between two ethoxycarbonyl groups.

the MO LCAO method in Hückel's approximation with B. Pullman and A. Pullman's parameters [4] were taken from our previous paper [2].



Geometry of the Porphyrin Molecule.

The calculation of the chemical shifts was made from the formula:

$$\Delta\tau = aE_z + bE^2,$$

where E_z is the component of the electric field $\vec{E}$ in the direction of the C—H bond.

The values of the constants a and b proposed by Musher [5] on the basis of an analysis of the theortical and experimental data are, respectively, $-2.9 \cdot 10^{-6}$ (stat V/cm)$^{-1}$ and $-7.38 \cdot 10^{-13}$ (stat V/cm)$^{-2}$.

The geometry of the porphyrin molecule according to Welb and Fleisher [6] is shown in the figure. The atoms the charges of which were considered in the calculation are denoted in this figure by the numbers 1–9.

The results of the calculations of the chemical shifts are given in the table. It also gives the contributions to the chemical shift of the meso-protons from the ring currents of the π-electrons calculated previously by McWeeny's method [3].

The greatest difference between the calculated and experimental figures is found for compounds II and IIIa. The cause of this may be a difference in their interaction with the polar solvent, since the molecules of II and IIIa possess higher dipole moments than those of the other compounds. On the other hand, the simplifications of Hückel's method and, as a consequence of these simplifications, the neglect of the effects of the polarization of the σ-bonds by the heteroatoms, which corresponds, from the results of semiempirical MO SCF calculations, to a considerable part of the total dipole moment of the C=O group, must lead to deviations that are general for all the compounds considered [7, 8].

The figures given in the table permit the conclusion that the shift of the signals from meso-protons taking place on the introduction of ethoxycarbonyl substituents into the β-position are due mainly to the change in the distribution of the π-electronic charges.

The results of the computing procedure given may be useful both in the identification of various porphyrins substituted in the β-position by substituents with carbonyl groups and also for the solution of the inverse question—the evaluation of charges from the chemical shifts shifts of the meso-protons.

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