ELECTRONIC STRUCTURE OF PORPHYRINS WITH ELECTRONEGATIVE SUBSTITUENTS

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Using the MO LCAO method in Hückel's approximation, the π-electronic charges and the bond orders of porphyrins containing ethoxycarbonyl and methyl substituents in the β-positions have been calculated. A correlation has been observed between the frequencies of stretching vibrations of the C=O groups in the IR spectra and the orders of their bonds. Changes in the chemical shifts of the protons of the methyl groups with the introduction of ethoxycarbonyl substituents agree with the changes in the π-electron charges.

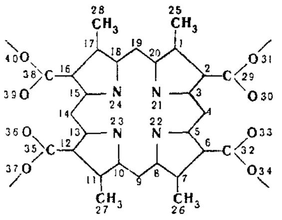
Continuing earlier investigations on the influence of electronegative substituents on the physicochemical properties of the porphyrins [1, 2], in the present paper using the MO LCAO method in Hückel's approximation, we have calculated the π-electron charges and the bond orders for the following porphyrins: 1,4,5,8-tetramethylporphyrin (I), 2-ethoxycarbonyl-1,4,5,8-tetramethylporphyrin (II), 2,3-diethoxycarbonyl-1,4,5,8-tetramethylporphyrin (IIIa), 2,6-diethoxycarbonyl-1,4,5,8-tetramethylporphyrin (IIIb), 2,7-diethoxycarbonyl-1,4,5,8-tetramethylporphyrin (IIIc), 2,3,6-triethoxycarbonyl-1,4,5,8-tetramethylporphyrin (IV), and 2,3,6,7-tetraethoxycarbonyl-1,4,5,8,tetramethylporphyrin (V). The results of the calculations are used to discuss the IR frequencies of the vibrations of the C=O groups and also the NMR spectra.

METHOD OF CALCULATION

In the MO LCAO method in Hückel's approximation, the π-electron charge on an atom r is given by the expression: $q_r = \sum_i c_{ir}^2 n_i$, where c_{ir} are the coefficients of the molecular orbitals, n_i is the number of electrons in the i-th molecular orbital; and the bond order $p_{rs} = \sum_i c_{ir} c_{is} n_i$.

As in the preceding papers [1, 2], we used a set of semiempirical parameters [3]. The resonance integral for the bond between the ethoxycarbonyl group and the porphyrin ring was chosen in such a way as to ensure a linear relationship between the experimental and the calculated energies of the π—π transitions [1, 2].

The results of the calculations of the electron densities are given in Tables 1–4. The system of numbering the atoms is given in the following scheme:



INFRARED SPECTRA

Coulson and Longuet-Higgins [4] have established that the frequency of the stretching vibrations of the bond rs is determined by the force constant

$$K_{rs} = \xi p_{rs} + \sigma(1 - p_{rs}) + \left[\frac{\xi\sigma(s-d)}{\xi p_{rs} + \sigma(1 - p_{rs})} \right]^2 \frac{\pi_{rs,rs}}{2},$$

where $\pi_{rs;rs}$ is the self-polarizability and p_{rs} is the order of the bond rs, ξ and σ are the force constants of double and single bonds, and d and s are the lengths of these bonds. For the C=O bond, the self-polarizability is found to have a very small influence [5] and therefore we may take $k_{rs} = \xi p_{rs} + \sigma(1 - p_{rs})$.

Since a good correlation has been observed by a number of investigators [5–7] between the frequencies of the stretching vibrations of the carbonyl groups of various unsaturated compounds and the orders of their bonds, it was natural to expect a similar correlation in the case of the porphyrins. Table 5 gives a comparison of the experimental frequencies of the stretching vibrations of the C=O groups with the orders of the C=O bonds for compounds II–V. The IR spectra were taken in KBr tablets on a UR-10 spectrometer.

In a consideration of the IR frequencies of the porphyrins II–V, they could have been expected to change, both because of the mutual influence of the ethoxycarbonyl substituents through the conjugated porphyrin ring, and also because of steric hindrance, which we took into account in the calculations by means of the experimental data on electronic absorption spectra [1, 2]. Calculations showed that the first effect has a slight influence on the order of the bonds of the C=O groups. Thus, only two vibrational frequencies are predicted, a lower one for the C=O groups of the ethoxycarbonyl substituents not subject to steric hindrance and a higher one for the case where there is steric hindrance. The values of these frequencies are about 1695 and 1715 cm^{-1}. Deviations from these values are easily explained by the experimental error. The broad band at 1700–1709 cm^{-1} apparently arises as a consequence of the superposition of the two bands mentioned. Compound V forms an exception; this should have an absorption band at about 1715 cm^{-1}.

CHEMICAL SHIFTS OF THE PROTONS OF THE METHYL GROUPS

In experiments on nuclear magnetic resonance, a nucleus with a magnetic moment gives a signal corres-

Table 1

π-Electronic Charges for Porphyrins with Ethoxycarbonyl Substituents in the Form of the Free Bases

Atom No.	Compound						
	I	II	IIIa	IIIb	IIIc	IV	V
1	0.906	0.852	0.860	0.852	0.852	0.860	0.860
2	1.142	1.155	1.154	1.154	1.155	1.153	1.153
3	1.006	0.994	0.993	0.994	0.993	0.993	0.993
4	0.964	0.972	0.978	0.967	0.967	0.973	0.970
5	1.006	1.003	0.993	1.002	1.002	0.993	0.993
6	1.142	1.143	1.154	1.142	1.142	1.154	1.153
7	0.906	0.905	0.860	0.904	0.905	0.860	0.860
8	1.035	1.034	1.035	1.034	1.032	1.035	1.034
9	0.935	0.934	0.929	0.929	0.933	0.924	0.924
10	1.035	1.033	1.034	1.035	1.032	1.035	1.034
11	0.906	0.906	0.906	0.852	0.905	0.852	0.860
12	1.142	1.141	1.141	1.155	1.142	1.154	1.153
13	1.006	1.006	1.005	0.994	1.002	0.993	0.993
14	0.964	0.959	0.955	0.967	0.967	0.964	0.970
15	1.006	1.005	1.005	1.002	0.993	1.002	0.993
16	1.142	1.141	1.141	1.142	1.155	1.141	1.153
17	0.906	0.906	0.906	0.904	0.852	0.904	0.860
18	1.035	1.035	1.034	1.034	1.036	1.033	1.034
19	0.935	0.929	0.929	0.929	0.924	0.929	0.924
20	1.035	1.036	1.035	1.035	1.036	1.034	1.034
21	1.512	1.493	1.498	1.491	1.491	1.496	1.494
22	1.512	1.514	1.498	1.511	1.512	1.495	1.494
23	1.512	1.511	1.509	1.491	1.512	1.489	1.494
24	1.512	1.510	1.509	1.511	1.491	1.510	1.494
25	1.950	1.943	1.944	1.943	1.943	1.944	1.944
26	1.950	1.950	1.944	1.949	1.950	1.944	1.944
27	1.950	1.950	1.950	1.943	1.950	1.943	1.944
28	1.950	1.950	1.950	1.949	1.943	1.949	1.944
29		0.774	0.768	0.774	0.774	0.768	0.768
30		1.390	1.382	1.390	1.390	1.381	1.381
31		1.926	1.925	1.926	1.926	1.925	1.925
32			0.768			0.768	0.768
33			1.382			1.382	1.381
34			1.925			1.925	1.925
35				0.774		0.774	0.768
36				1.390		1.390	1.381
37				1.926		1.926	1.925
38					0.774		0.768
39					1.390		1.381
40					1.926		1.925

Table 2

π-Electronic Charges for Porphyrins with Ethoxycarbonyl Substituents in the form of Dications

Atom No.	Compound						
	I	II	IIIa	IIIb	IIIc	IV	V
1	2	3	4	5	6	7	8
1	0.869	0.826	0.831	0.826	0.825	0.831	0.831
2	1.077	1.100	1.098	1.097	1.098	1.095	1.094
3	0.979	0.962	0.961	0.962	0.962	0.961	0.961
4	0.928	0.940	0.948	0.931	0.931	0.939	0.934
5	0.979	0.974	0.961	0.974	0.974	0.961	0.961
6	1.077	1.080	1.098	1.077	1.077	1.096	1.094
7	0.869	0.866	0.831	0.866	0.867	0.831	0.831
8	1.012	1.010	1.012	1.009	1.077	1.011	1.009
9	0.904	0.902	0.898	0.897	0.900	0.893	0.892
10	1.012	1.009	1.009	1.011	1.007	1.011	1.009
11	0.869	0.869	0.869	0.826	0.867	0.826	0.831
12	1.077	1.074	1.072	1.097	1.007	1.096	1.094
13	0.979	0.979	0.979	0.962	0.974	0.962	0.961
14	0.928	0.920	0.914	0.931	0.931	0.926	0.934
15	0.979	0.979	0.979	0.974	0.962	0.974	0.961
16	1.077	1.075	1.072	1.077	1.098	1.075	1.094
17	0.869	0.869	0.869	0.866	0.825	0.866	0.831
18	1.012	1.011	1.009	1.009	1.013	1.007	1.009
19	0.904	0.898	0.898	0.897	0.893	0.896	0.892
20	1.012	1.014	1.012	1.011	1.013	1.010	1.009
21	1.700	1.689	1.691	1.687	1.687	1.690	1.688
22	1.700	1.701	1.691	1.699	1.699	1.689	1.688
23	1.700	1.698	1.697	1.687	1.699	1.686	1.688
24	1.700	1.698	1.697	1.699	1.687	1.698	1.688
25	1.947	1.941	1.942	1.941	1.941	1.942	1.942
26	1.947	1.946	1.942	1.946	1.946	1.942	1.942
27	1.947	1.947	1.947	1.941	1.946	1.941	1.942
28	1.947	1.947	1.947	1.946	1.941	1.946	1.942
29		0.771	0.766	0.771	0.771	0.765	0.765
30		1.380	1.373	1.380	1.380	1.373	1.372
31		1.926	1.925	1.926	1.926	1.925	1.925
32			0.766			0.765	0.765
33			1.373			1.373	1.372
34			1.925			1.925	1.925
35				0.771		0.771	0.765
36				1.380		1.379	1.372
37				1.926		1.926	1.925
38					0.771		0.765
39					1.379		1.372
40					1.926		1.925

Table 3

Bond Orders for Porphyrins with Ethoxycarbonyl Substituents in the Form of the Free Bases

Bond	Compound						
	I	II	IIIa	IIIb	IIIc	IV	V
1	2	3	4	5	6	7	8
1—2	0.735	0.684	0.693	0.684	0.683	0.693	0.693
2—3	0.520	0.486	0.492	0.486	0.486	0.491	0.492
3—4	0.588	0.592	0.591	0.592	0.591	0.591	0.590
4—5	0.588	0.588	0.591	0.586	0.588	0.590	0.590
5—6	0.520	0.519	0.492	0.519	0.519	0.492	0.492
6—7	0.735	0.735	0.693	0.735	0.735	0.693	0.693
7—8	0.495	0.493	0.497	0.494	0.493	0.497	0.497
8—9	0.597	0.599	0.598	0.599	0.598	0.598	0.597
9—10	0.597	0.596	0.595	0.595	0.598	0.595	0.597
10—11	0.495	0.495	0.495	0.499	0.493	0.499	0.497
11—12	0.735	0.735	0.734	0.684	0.735	0.683	0.693
12—13	0.520	0.519	0.520	0.486	0.519	0.486	0.492
13—14	0.588	0.589	0.588	0.592	0.588	0.591	0.590
14—15	0.588	0.587	0.588	0.586	0.591	0.587	0.590
15—16	0.520	0.520	0.520	0.519	0.486	0.519	0.492
16—17	0.735	0.734	0.734	0.735	0.683	0.735	0.693
17—18	0.495	0.495	0.495	0.494	0.499	0.493	0.497
18—19	0.597	0.597	0.595	0.599	0.596	0.597	0.597
19—20	0.597	0.597	0.598	0.595	0.596	0.597	0.597
20—1	0.495	0.499	0.497	0.499	0.499	0.497	0.497
20—21	0.501	0.500	0.499	0.501	0.500	0.501	0.501
21—3	0.506	0.522	0.520	0.522	0.523	0.519	0.520
22—5	0.506	0.507	0.520	0.508	0.506	0.521	0.520
22—8	0.501	0.500	0.499	0.500	0.501	0.499	0.501
23—10	0.501	0.502	0.503	0.501	0.501	0.501	0.501
23—13	0.506	0.506	0.507	0.522	0.506	0.522	0.520
24—15	0.506	0.507	0.507	0.508	0.523	0.507	0.520
24—18	0.501	0.501	0.503	0.500	0.500	0.502	0.501
25—1	0.229	0.249	0.246	0.249	0.249	0.246	0.246
26—7	0.229	0.230	0.246	0.230	0.230	0.246	0.246
27—11	0.229	0.229	0.229	0.249	0.230	0.249	0.246
28—17	0.229	0.229	0.229	0.230	0.249	0.230	0.246
29—2		0.340	0.309	0.340	0.340	0.309	0.309
29—30		0.849	0.860	0.849	0.849	0.860	0.860
29—31		0.297	0.301	0.297	0.297	0.301	0.301
32—6			0.309			0.309	0.309
32—33			0.860			0.860	0.860
32—34			0.301			0.301	0.301
35—12				0.340		0.340	0.309
35—36				0.849		0.849	0.860
35—37				0.297		0.297	0.301
38—16					0.340		0.309
38—39					0.849		0.860
38—40					0.297		0.301

Table 4

Bond Order for Porphyrins with Ethoxycarbonyl Substituents in the Form of Dications

Bond	Compound						
	I	II	IIIa	IIIb	IIIc	IV	V
1	2	3	4	5	6	7	8
1—2	0.696	0.656	0.664	0.656	0.655	0.664	0.663
2—3	0.567	0.534	0.539	0.534	0.535	0.539	0.540
3—4	0.595	0.599	0.599	0.599	0.597	0.599	0.597
4—5	0.595	0.595	0.599	0.593	0.595	0.597	0.597
5—6	0.567	0.566	0.539	0.567	0.566	0.540	0.540
6—7	0.696	0.697	0.664	0.696	0.697	0.663	0.663
7—8	0.532	0.529	0.528	0.531	0.530	0.530	0.530
8—9	0.607	0.611	0.612	0.607	0.607	0.609	0.607
9—10	0.607	0.604	0.602	0.607	0.607	0.605	0.607
10—11	0.532	0.533	0.534	0.531	0.530	0.532	0.530
11—12	0.696	0.695	0.694	0.656	0.697	0.655	0.663
12—13	0.567	0.567	0.568	0.534	0.566	0.535	0.540
13—14	0.595	0.595	0.593	0.599	0.595	0.597	0.597
14—15	0.595	0.593	0.593	0.593	0.597	0.594	0.597
15—16	0.567	0.568	0.568	0.567	0.535	0.567	0.540
16—17	0.696	0.695	0.694	0.696	0.655	0.696	0.663
17—18	0.532	0.533	0.534	0.531	0.532	0.531	0.530
18—19	0.607	0.604	0.602	0.607	0.607	0.605	0.607
19—20	0.607	0.610	0.612	0.607	0.607	0.609	0.607
20—1	0.532	0.530	0.528	0.531	0.532	0.529	0.530
21—20	0.411	0.412	0.410	0.414	0.413	0.413	0.414
21—3	0.418	0.432	0.431	0.433	0.433	0.431	0.431
22—5	0.418	0.419	0.431	0.420	0.419	0.431	0.431
22—8	0.411	0.410	0.410	0.411	0.412	0.412	0.414
23—10	0.411	0.413	0.414	0.414	0.412	0.415	0.414
23—13	0.418	0.418	0.419	0.433	0.419	0.433	0.431
24—15	0.418	0.419	0.419	0.420	0.433	0.420	0.431
24—18	0.411	0.413	0.414	0.411	0.413	0.413	0.414
25—1	0.240	0.256	0.254	0.256	0.256	0.254	0.254
26—7	0.240	0.241	0.254	0.241	0.241	0.254	0.254
27—11	0.240	0.240	0.240	0.256	0.256	0.256	0.254
28—17	0.240	0.240	0.240	0.241	0.241	0.241	0.254
29—2		0.326	0.295	0.326	0.326	0.295	0.295
29—30		0.855	0.865	0.855	0.855	0.865	0.865
29—31		0.299	0.302	0.299	0.299	0.302	0.302
32—6			0.295			0.295	0.295
32—33			0.865			0.865	0.865
32—34			0.302			0.302	0.302
35—12				0.326		0.325	0.295
35—36				0.855		0.855	0.865
35—37				0.299		0.299	0.302
38—16					0.326		0.295
38—39					0.855		0.865
38—40					0.299		0.302

Table 5

Correlation Between the Frequencies of the Stretching Vibrations of the C=O Groups and the Bond Orders of the Porphyrins

Compound	$\nu_{C=O}$, cm^{-1}	$P_{C=O}$ (free bases) for the bonds			
		29—30	32—33	35—36	38—39
II	1697	0.849			
IIIa	1715	0.860	0.860		
IIIb	1694	0.849		0.849	
IIIc	1695	0.849			0.849
IV	1700—1709	0.860	0.860	0.849	
V	1700—1710	0.860	0.860	0.860	0.860

Table 6

Chemical Shifts of the Protons of the Methyl Groups δ and Excess π-Electronic Charges Δq

Compound	δ, ppm from TMS (number of protons)		Δq on the methyl groups (dications)			
I	3.81 (12)		0.0534	0.0534	0.0534	0.0534
II	3.79 (9)	4.06 (3)	0.0587	0.0537	0.0534	0.0534
III a	3.79 (6)	4.02 (6)	0.0581	0.0581	0.0534	0.0534
III c	3.75 (6)	4.02 (6)	0.0587	0.0537	0.0537	0.0587
IV	3.73 (3)	4.02 (9)	0.0581	0.0581	0.0586	0.0537
V		3.98 (12)	0.0580	0.0580	0.0580	0.0580

ponding to the value of the magnetic field at the nucleus $H = (1 - \sigma)H_0$, where H_0 is the applied field and σ is the screening constant. Where the molecule contains polar groups, the proton H attached to an atom X will have an additional chemical shift [8]: $\Delta\delta = -aE_Z - bE^2$, where E_Z is the component of the electric field $\vec{E}$ created by the polar groups in the X—H direction. In this expression, the main member is that which depends linearly on the field strength. A linear relationship between the chemical shift of a proton and the excess of π-electronic charge on the carbon atom to which the proton is attached has been observed for many unsaturated compounds [9–11]. We have established a similar correlation for the porphyrins I–V.

The proton resonance spectra of these compounds in the form of dications were taken on an INM-C-60 spectrometer. Trifluoroacetic acid was used as the solvent and the concentration of solute was about 15 mg/ml. Tetramethylsilane was used as internal standard.

In the spectra obtained for all the compounds, the protons of the methyl groups gave not more than two signals. One of them corresponds to methyl groups attached to pyrrole rings with a free β-position and the other signal appears when an exthoxycarbonyl substituent is present in the β-position. Since, in the calculation of these electron densities, the model of a heteroatom was used for the methyl groups, the charges on the methyl groups are compared with the experimental data.

It can be seen that (with an accuracy of 5×10^{-4}) calculation gives two values of the charges on the CH_3 groups. The methyl groups with a greater positive charge (adjacent to ethoxycarbonyl groups) have a lower screening constant and, accordingly, give a signal at a smaller value of the field.

In this work, the influence of π-electron currents on the chemical shifts is not discussed. A quantum mechanical calculation has shown that for the series of porphyrins I–V the contribution of the π-electron currents to the chemical shifts of the methyl protons is constant within the limits of experimental accuracy and does not change the quantitative picture of the proton resonance spectra.

The comparison of the calculated and experimental values for the IR spectra and the PMR spectra that has been carried out shows that the simple Hückel method correctly predicts the qualitative change in the electronic structure of the porphyrins on the introduction of different numbers of similar electronegative substituents. In conclusion, we may mention that, according to calculation, the introduction of an ethoxycarbonyl substituent into the β-position of 1,4,5,8-tetramethylporphyrin has a relatively weak influence on the π-electron charges and the indices of the free valence of the unsubstituted β-positions. A considerable change in the electron densities takes place in the meso positions. Thus, for all the free β-positions the difference in reactivity determined by electron densities is far less than for the meso positions.

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