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QUANTUM CHEMICAL CALCULATIONS OF THE MOLECULAR STRUCTURE OF PYRROLE DERIVATIVES BY THE PARISER–PARR–POPLE METHOD

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SUMMARY

The molecular structure of pyrrole derivatives has been studied by means of quantum chemical calculations. Calculations were performed by the modified Pariser–Parr–Pople method. Results obtained with the method of Del Re for the σ-system served as starting point for the calculation of the π-bond systems. The effective nuclear charges were determined according to Burns. Exponential relationships were used for the calculation of ionisation energies. In the calculation of the singlet and triplet transitions, consideration has been given to the configuration interactions. The partial charges, bond orders, linear coefficients, eigen values, singlet and triplet transition values, oscillator strength and dipole moment have been determined. Results of these calculations are in good agreement with experimental data of the UV absorption spectra and dipole moments.

INTRODUCTION

In our recent work[1] quantum chemical calculations were carried out for pyrrole and *N*-(trimethylsilyl)pyrrole molecules. For the σ-bond systems the approximation method of Del Re has been used, while the π-bond system has been studied by the extended Hückel method. Our present work discusses the results of calculations made for pyrrole derivatives by the Pariser–Parr–Pople method, *i.e.* the LCAO–MO–SCF–PPP–CI method.

THE PPP METHOD

The coulomb integral was calculated on the basis of the PPP method[2,3] using the following relationship:

$$\alpha_i = U_i + \tfrac{1}{2} q_i \cdot \gamma_{ii} + \sum_{i \neq j} (q_j - n_j) \cdot \gamma_{ij} \text{ eV}$$

where:
α_i is the coulomb integral of the i-th atom;
U_i is the ionisation energy in the corresponding valence state;

q_i, q_j is the electron density of the i-th and j-th atom, respectively;
n_j is the number of electrons donated by the atom j to the π-system;
γ_{ii} and γ_{ij} are the empirical values of the $[ii/ii]$ single center and the $[ii/jj]$ bicenter integrals, respectively. The γ_{ii} values were taken from the literature[4,5], whereas γ_{ij} was calculated using the relationships of Mataga and Nishimoto[6]:

$$\gamma_{ij} = \frac{14.397}{a_{ij}+R_{ij}}$$

$$a_{ij} = 2\frac{14.397}{\gamma_{ii}+\gamma_{jj}}$$

where R_{ij} is the bond distance in Å.

The ionisation energy was determined as a function of the effective nuclear charge. In our calculations, the effective nuclear charges of Burns have been used[7] instead of Slater's effective nuclear charges. Burns makes distinctions between the shielding factors of the s, p, d, and f electrons. While Slater's method gave highly real values for the effective nuclear charge of d orbitals, this value is determined considerably more accurately by the method of Burns. In the determination of the shielding parameters, promotional and hybridization states have also been considered. For the ionisation energies in function of Z, parabolic relationships are published in the literature[8]. Instead of these, however, it is more correct to use exponential curves, which will be described in detail in a later work. This exponential function changes in a monotonic form and can be fitted more exactly to the experimental ionisation energies. Owing to the above mentioned reason, relationships of the form

$$U = A \cdot e^{B \cdot Z}$$

have been determined, partly by the transformation of the parabolic relationships published in the literature, and partly from experimental results. These relationships are as follows:

$$U_{\mathrm{C}} = 0.61329 \cdot e^{1.036616\,Z}$$
$$U_{\mathrm{N}^+} = 3.9326 \cdot e^{0.54675\,Z}$$
$$U_{\mathrm{Si}} = 0.20662 \cdot e^{0.955552\,Z}$$

In the calculation of the effective nuclear charge of an atom in a given molecule, the δ_σ partial charges obtained with the method of Del Re, and the q_π-electron densities resulting from the calculations of the π-system have been taken into consideration. Thus, the actual effective nuclear charge was calculated in the following way:

$$Z = Z^0 + 0.35\delta_\sigma - 0.35q_\pi$$

Exchange integral values were calculated on the basis of the work of Helmholtz and Wolfsberg[9] as follows:

$$\beta_{ij} = \tfrac{1}{2}k \cdot (U_i + U_j) \cdot S_{ij} \text{ eV}$$

where S_{ij} is the overlap integral, which can be calculated by means of an integral table[10], when R_{ij}, Z_i and Z_j are known.

The value of the factor of proportionality was determined from the data for ethylene[11]:

$$\beta_{CC} = -3.05 \quad \text{eV}$$
$$S_{CC} = 0.366783 \quad \text{eV}$$

and from these:

$$k = 0.7637$$

Singlet and triplet transitions were calculated as follows:

$$^1E_{ab} = e_b - e_a - J_{ab} + 2K_{ab}$$
$$^3E_{ab} = e_b - e_a - J_{ab}$$
$$J_{ab} = \sum_i \sum_j c_{ai}^2 \cdot c_{bi}^2 \cdot \gamma_{ij}$$
$$K_{ab} = \sum_i \sum_j c_{ai} \cdot c_{bj} \cdot c_{bi} \cdot c_{bj} \cdot \gamma_{ij}$$

where:

J_{ab} is the coulomb-electron interaction integral;
K_{ab} is the exchange-electron interaction integral;
c is the linear coefficient.

Relationships used for the calculation of configuration interaction (CI) are:

$$^1E_{ab}^{cd} = c_1^2 \cdot {}^1E_{ab} + c_2^2 \cdot {}^1E_{cd} \pm 2c_1 \cdot c_2 \cdot {}^1H_{ab}^{cd}$$
$$^3E_{ab}^{cd} = c_1^2 \cdot {}^3E_{ab} + c_2^2 \cdot {}^3E_{cd} \pm 2c_1 \cdot c_2 \cdot {}^3H_{ab}^{cd}$$
$$^1H_{ab}^{cd} = -J_{ab}^{cd} + 2K_{ab}^{cd}$$
$$^3H_{ab}^{cd} = -J_{ab}^{cd}$$
$$J_{ab}^{cd} = \sum_i \sum_j c_{ai} \cdot c_{ci} \cdot c_{bj} \cdot c_{dj} \cdot \gamma_{ij}$$
$$K_{ab}^{cd} = \sum_i \sum_j c_{ai} \cdot c_{cj} \cdot c_{bi} \cdot c_{dj} \cdot \gamma_{ij}$$

The oscillator strength is calculated from the following relationships:

$$f = 1.085 \cdot 10^{-5} \cdot v \cdot D \cdot G$$
$$D = (Q_x^{cl})^2 + (Q_y^{cl})^2 + (Q_z^{cl})^2$$
$$Q_x^{cl} = \sum_{a,b} c_{ab} Q_x^{ab}$$
$$Q_x^{ab} = \sqrt{2} \sum_i c_{ai} \cdot c_{bi} \cdot R_{xi}$$

where:

f is the oscillator strength
v is the transition frequency of the singlet determined by the configuration interaction
D is the dipole field strength
Q_x is the component x of the transition dipole moment
G is the degree of degeneration (in our case 1)
c_{ab} are the linear coefficients of the configuration interaction
c_{ai}, c_{bi} are linear coefficients
R_{xi} is the x space co-ordinate of the i-th atom.

RESULTS

Our calculations were performed for the following compounds: pyrrole (I), 1-tert-butylpyrrole (II), 2,5-dimethylpyrrole (III), 1-(trimethylsilyl)pyrrole (IV), 1-(trimethylsilyl)-2,5-dimethylpyrrole (V). Results of our Del Re calculations for the σ-bond system are listed in Table 1. Values of the bond distances were taken from literature[12,13].

TABLE 1

δ_σ PARTIAL CHARGES AND μ_σ DIPOLE MOMENTS OF PYRROLE DERIVATIVES, CALCULATED BY THE METHOD OF DEL RE

Compound	δ_{Si}	δ_N	δ_C	δ_C	μ_σ
(I)		−0.4695	+0.0513	−0.0315	0.1012
(II)		−0.2974	+0.0385	−0.0328	0.1231
(III)		−0.4568	+0.0277	−0.0229	0.2657
(IV)	−0.3144	−0.3969	−0.0336	−0.0333	0.7698
(V)	+0.3155	−0.3836	−0.0110	−0.0248	0.9367

For the single center integrals the following empirical values were used:

$\gamma_{CC} = 7.3783$ eV (referred to ethylene)
$\gamma_{NN} = 17.44$ eV (ref. 4)
$\gamma_{SiSi} = 3.762$ eV (ref. 5)

Starting data for the calculations performed by the PPP method for the π-bond system of the single compounds are listed in Table 2.

The electronic computer Model RAZDAN-3 of the Technical University of Budapest was used for the calculations. The values of Z_i, U_i and α_i were changed by means of the results obtained in the zeroeth approximation, while the values of β_{ij} were kept constant. Approximations were continued until self-consistency. The δ_π partial charges and the p_π bond orders obtained for the single compounds are shown in Figs. 1 and 2, and eigen values are listed in Table 3.

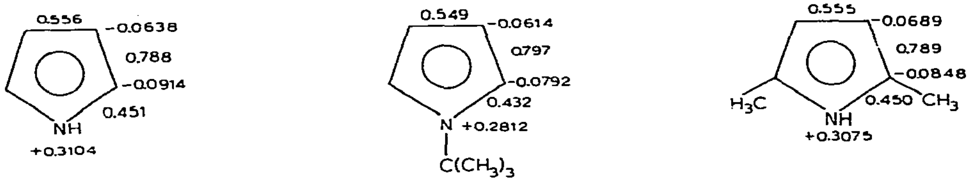

Fig. 1. π-partial charges and π-bond orders of pyrrole, 1-tert-butylpyrrole and 2,5-dimethylpyrrole.

Energy values of the ${}^1E_{CI}$ singlet and ${}^3E_{CI}$ triplet transitions, calculated by the methods of configuration interaction, are listed in Table 4.

Oscillator strengths were calculated on the basis of the relationships given above. Owing to the symmetry of the molecules, values of the Q_y and Q_z components were zero. Oscillator strength values are listed in Table 5.

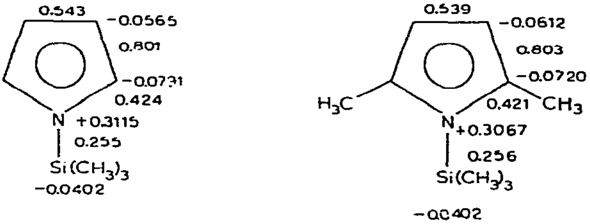

Fig. 2. π-partial charges and π-bond orders of 1-(trimethylsilyl)pyrrole and 1-(trimethylsilyl)-2,5-dimethylpyrrole.

TABLE 2

STARTING DATA FOR THE CALCULATION OF THE π-BOND SYSTEM OF PYRROLE DERIVATIVES BY THE PPP METHOD

Compound	Z_{Si}	Z_N	Z_C	Z_C
(I)		3.636	2.818	2.789
(II)		3.696	2.813	2.789
(III)		3.640	2.810	2.792
(IV)	1.860	3.661	2.812	2.788
(V)	1.860	3.666	2.804	2.791

Compound	U_{Si}	U_N	U_C	U_C (eV)
(I)		−28.710	−11.370	−11.033
(II)		−29.599	−11.311	−11.033
(III)		−28.768	−11.276	−11.068
(IV)	−1.2219	−29.076	−11.299	−11.022
(V)	−1.2219	−29.150	−11.206	−11.056

Compound	β_{SiN}	β_{NC}	β_{CC}	β_{CC} (eV)
(I)		−2.5599	−2.9250	−2.7808
(II)		−2.5960	−2.9172	−2.7808
(III)		−2.5664	−2.9172	−2.7755
(IV)	−1.5743	−2.5836	−2.9143	−2.7781
(V)	−1.5780	−2.5773	−2.9212	−2.7725

TABLE 3

EIGEN-VALUES OF PYRROLE DERIVATIVES IN eV

Compound	E_1	E_2	E_3	E_4	E_5	E_6
(I)	−17.5925	−12.7872	−11.4012	−2.1807	−0.4468	
(II)	−18.0028	−12.9001	−11.3634	−2.2323	−0.4424	
(III)	−17.6075	−12.7856	−11.3500	−2.1466	−0.4435	
(IV)	−18.0306	−13.0030	−11.4569	−2.7316	−1.1710	−0.5422
(V)	−18.0334	−13.0101	−11.4202	−2.7016	−1.1615	−0.5273

EVALUATION

The results of our calculations, performed by the Del Re and Pariser–Parr–Pople methods for pyrrole derivatives, have been evaluated by comparing them with experimental dipole moment data and data of ultraviolet absorption spectra. Table

TABLE 4

ENERGY VALUES OF THE ${}^1E_{C1}$ SINGLET AND ${}^3E_{C1}$ TRIPLET TRANSITIONS OF PYRROLE DERIVATIVES

Compound	${}^1E_1$	${}^1E_2$	${}^1E_3$	${}^1E_4$	${}^1E_5$	${}^1E_6$	${}^1E_7$	${}^1E_8$	${}^1E_9$
(I)	5.9516	7.2600	7.8108	8.9044	11.3793	12.9658			
(II)	5.9043	7.3010	7.7824	9.0312	11.6633	13.3288			
(III)	5.9395	7.2745	7.7775	8.9070	11.4195	12.9754			
(IV)	5.7053	7.0313	7.4663	7.7362	8.9112	9.0517	11.2385	13.1919	13.2830
(V)	5.7032	7.0651	7.4391	7.7230	8.9295	9.0694	11.2579	13.1941	13.2933

Compound	${}^3E_1$	${}^3E_2$	${}^3E_3$	${}^3E_4$	${}^3E_5$	${}^3E_6$	${}^3E_7$	${}^3E_8$	${}^3E_9$
(I)	4.1491	5.2327	6.3882	7.3138	9.4369	12.6117			
(II)	4.0682	5.3801	6.4627	7.4386	9.7171	13.0198			
(III)	4.1337	5.2739	6.3565	7.3173	9.4690	12.6254			
(IV)	3.9554	5.3402	6.4677	7.3464	7.5094	8.4894	9.7223	12.5996	12.9740
(V)	3.9556	5.3737	6.4649	7.3289	7.5251	8.5106	9.7593	12.5962	12.9856

TABLE 5

CALCULATED OSCILLATOR STRENGTHS OF PYRROLE DERIVATIVES

Compound	f
(I)	0.509
(II)	0.497
(III)	0.507
(IV)	0.418
(V)	0.413

TABLE 6

COMPARISON OF THE CALCULATED AND MEASURED DIPOLE MOMENTS OF PYRROLE DERIVATIVES

Compound	μ_σ (D)	μ_π (D)	$\mu_{\sigma\pi}$ (D)	μ_{exp} (D)	Difference (D)
(I)	0.101	1.983	2.084	1.83^{14}	−0.254
(II)	0.123	1.842	1.965	1.835^{15}	−0.130
(III)	0.266	2.037	2.303	2.064^{15}	−0.239
(IV)	0.770	1.399	2.169	2.224^{15}	+0.055
(V)	0.937	1.440	2.377		

6 shows the μ_σ and μ_π dipole moments calculated from the σ and π partial charges, the resulting dipole moment $\mu_{\sigma\pi}$ calculated from these dipole moments, and the difference between calculated and measured data.

Table 6 shows a good agreement between calculated and measured data. Differences are smaller than reported in our previous work[1] for calculations with the extended Hückel method.

In Table 7 the experimental ultraviolet absorption data of the pyrrole derivatives are compared with the calculated values of the ${}^1E_{C1}$ singlet transitions. Here also, calculated and measured results are in good agreement.

TABLE 7

COMPARISON OF THE MEASURED UV ABSORPTION MAXIMA[15] OF PYRROLE DERIVATIVES AND THEIR CALCULATED SINGLET ENERGY TRANSITIONS

Compound	λ_{max} (nm)	ν^* (eV)	$^1E_1$ (eV)	Difference (eV)
(I)	216	5.74	5.95	−0.21
(II)	216	5.74	5.90	−0.16
(III)	216	5.74	5.94	−0.20
(IV)	217	5.71	5.71	0.00
(V)	215	5.77	5.70	+0.07

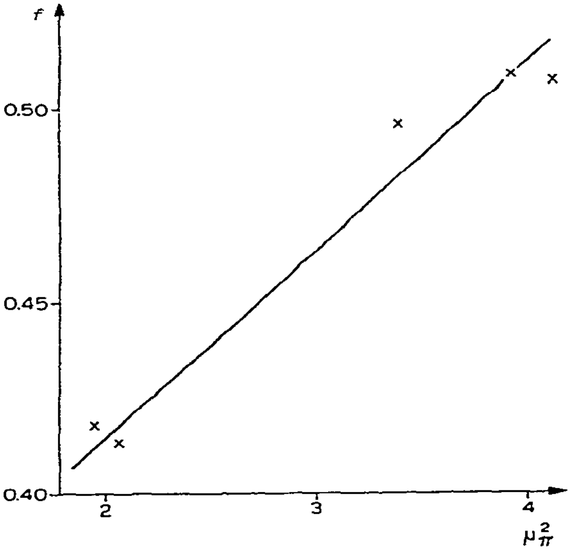

Fig. 3. Straight line of correlation between μ_π^2 and f.

Experimental oscillator strengths could not be calculated from the course of the UV spectra. Therefore, calculated theoretical values were compared with the square of the μ_π dipole moments. As a strict relationship exists between the oscillator strength and the transition dipole moment, and the transition and permanent dipole moments of our series of compounds are proportional to each other, in accordance with expectation, a correlation exists between the oscillator strength and μ_π^2. This correlation, expressed in a more precise form, corresponds to the extinction–dipole moment relationship, discussed in an earlier work[15]. The relationship between oscillator strength and dipole moment has been plotted in Fig. 3.

The results of our calculation support our initial assumption, according to which a d_π–p_π bond is formed between the silicon and the nitrogen atoms. The six electrons, participating in the delocalisation of the pyrrole ring, enter into interaction with the empty d orbitals of the silicon atom linked to the nitrogen, and six-electron, six-centered delocalised molecular orbitals are formed. For the π-bond order of the Si–N bond a value of 0.255 to 0.256 was obtained, which is in good agreement with the total bond order value of 1.20, calculated from IR data[16] using Siebert's formula.

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