Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CALCULATION OF THE MOLECULAR STRUCTURE OF PYRROLE AND *N*-(TRIMETHYLSILYL)PYRROLE ACCORDING TO THE DEL RE AND EXTENDED HÜCKEL METHODS

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(Received July 15th, 1969)

SUMMARY

Quantum chemical calculations have been carried out according to Del Re and Hückel for pyrrole and *N*-(trimethylsilyl)pyrrole during a study of the silicon–nitrogen bond. It was found that the Si–N bond is of d_π–p_π character and that the π-bond is of the order of 0.156. The results are in good agreement with ultraviolet spectra and dipole moments.

Ultraviolet spectra and dipole moments of pyrrole and *N*-substituted pyrrole derivatives have been recorded[1,2] in the course of a study of the silicon–nitrogen bond. The data obtained justify the conclusion that a d_π–p_π interaction also takes place between the silicon and nitrogen atoms. The silicon atom participates through its unoccupied *d*-orbitals, via the *p*-electrons of the nitrogen atom, in the delocalization of the pyrrole ring, and a system of six electrons and six centres results.

In this paper, Del Re calculations for the σ-bonding system in pyrrole and *N*-(trimethylsilyl)pyrrole molecules, and calculations (according to the extended Hückel method) for the π-systems will be described.

The approximation according to Del Re[3] was used for the calculation of σ-bonding. The use of the original method of calculation has been extended to molecules that contain silicon atoms. The δ^0-value for silicon has been determined and also the parameters of induction and resonance for Si–C and Si–N bonds[4]. Table 1 gives the data used in our calculations.

TABLE 1

DEL RE PARAMETERS

	C–C	C–H	C–N	N–H	Si–C	Si–N
ε_{AB}	1.00	1.00	1.00	0.45	0.90	0.75
$\gamma_{A(B)}$	0.1	−0.2	0.1	0.3	0.2	0.2
$\gamma_{B(A)}$	0.1	0.4	0.1	0.4	0.4	0.4
δ^0_A	sp^3: 0.07 sp^2: 0.12	sp^3: 0.07 sp^2: 0.12	sp^3: 0.07 sp^2: 0.12	sp^2: 0.30	−0.10	−0.10
δ^0_B	sp^3: 0.07 sp^2: 0.12	0.00	sp^2: 0.30	0.00	sp^3: 0.07 sp^2: 0.12	sp^2: 0.30

Calculations for pyrrole, *N*-tert-butylpyrrole, and *N*-(trimethylsilyl)pyrrole were carried out since the data for the molecular structure of these compounds are known[5]. The distribution of partial σ-charges, and the μ_σ dipole moment of these molecules were determined. The results of our calculations are shown in Fig. 1.

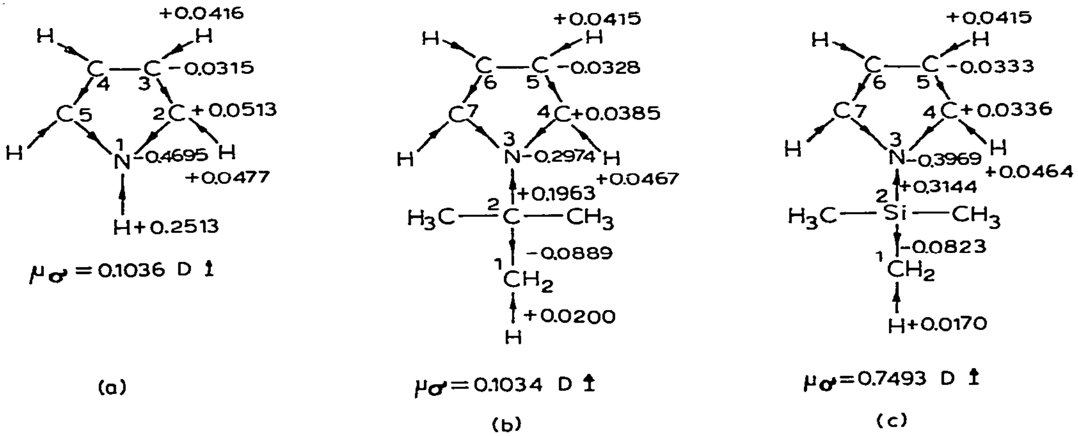


Fig. 1. Partial σ-charges, and μ_σ dipole moments of: (a) pyrrole; (b) *N*-tert-butylpyrrole; (c) *N*-(trimethylsilyl)pyrrole.

The arrows in Fig. 1 indicate the directions of the several σ-bond dipole vectors.

For the calculation of the π-bond systems the extended LCAO-MO method of Hückel[6] was adopted. Coulomb- and resonance-integrals were derived from ionization energies and bond lengths on the basis of tables compiled by Krugljak and Whitman[7]; 11.16 eV[8] was accepted as the ionization energy of carbon, 28.71 eV as that for nitrogen in pyrrole[9], and 2.07 eV[10] for silicon. Coulomb- and resonance-integrals in atomic units were determined from these data and then, based upon the coulomb integral of carbon in benzene and the resonance integral of a carbon–carbon bond in benzene, the integrals were written in parameter form. Starting with the zero'th approximation, the ω-technique was applied ($\omega = 1.4$), the probable end-point of the iteration was then determined by graphical extrapolation.

In the course of our calculations we determined the π-partial charges (δ), π-bonding orders (*p*), linear coefficients (*c*), eigen-values (*E*), the figures (Δm) for the π–π* transition, and the π dipole moment (μ_π). Table 2 lists the initial and final

TABLE 2

INITIAL INTEGRATION VALUES AND FINAL INTEGRATION VALUES AFTER ITERATION FOR PYRROLE

	Initial		Final
α_1	$\alpha + 1.3144\,\beta$		$\alpha + 1.8790\,\beta$
α_2	$\alpha + 0.5453\,\beta$		$\alpha + 0.3382\,\beta$
α_3	$\alpha - 0.0032\,\beta$		$\alpha - 0.0720\,\beta$
β_{12}		$1.1581\,\beta$	
β_{23}		$1.0179\,\beta$	
β_{34}		$0.9720\,\beta$	

TABLE 3

EIGEN-VALUES, LINEAR COEFFICIENTS AND THE FIGURES FOR THE π–π^* TRANSITION OF PYRROLE

	c_1	c_2	c_3	c_4	c_5
$E_1=\alpha+3.0694\ \beta$	0.7798	0.4007	0.1881	0.1881	0.4007
$E_2=\alpha+1.1352\ \beta$	0.4443	−0.1428	−0.6172	−0.6172	−0.1428
$E_3=\alpha+0.8774\ \beta$	0.0000	0.6248	0.3310	−0.3310	−0.6248
$E_4=\alpha-1.0873\ \beta$	0.4410	−0.5648	0.2893	0.2893	−0.5648
$E_5=\alpha-1.5833\ \beta$	0.0000	0.3310	−0.6248	0.6248	−0.3310
Δm			1.9647 β		

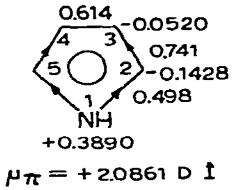
integration figures for pyrrole and Table 3 the eigen-values and linear coefficients obtained in the course of the calculations.

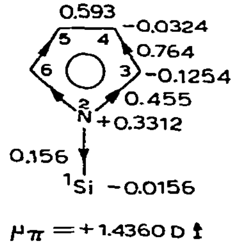
Figure 2 shows π partial charge distribution, π-bond orders, and π dipole moments. The arrows indicate the directions of the several π-bond dipole vectors.

Initial, and final data referring to the *N*-(trimethylsilyl)pyrrole molecule are listed in Tables 4, and 5, and in Fig. 3.

A parametric calculation using the method of Hückel gives correct values for bond order and partial charges and relative values for molecular orbital energies. Figure 4 shows the molecular orbital levels calculated for pyrrole and *N*-(trimethylsilyl)pyrrole.

The results of our calculations for σ- and π-systems suggest the following. Our values (1.9647 β/1.8524 β) for π–π^* transitions agree well with the slight batho-





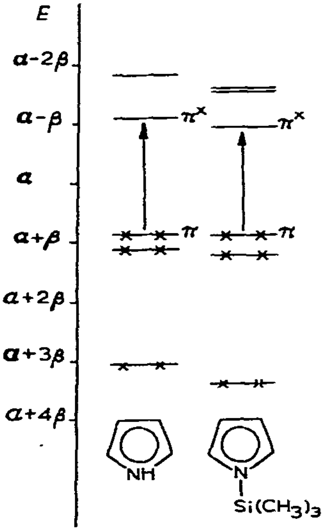


Fig. 2. Distribution of partial π-charges, the π-bond order, and the μ_π dipole moment, in pyrrole.

Fig. 3. Distribution of partial π-charges, the π-bond order, and the μ_π dipole moment, in *N*-(trimethylsilyl)-pyrrole.

Fig. 4. Molecular orbital levels of pyrrole and of *N*-(trimethylsilyl)pyrrole.

TABLE 4

INITIAL INTEGRATION VALUES AND FINAL INTEGRATION VALUES AFTER ITERATION FOR *N*-(TRIMETHYLSILYL)-PYRROLE

	Initial		Final
α_1	$\alpha-1.4805\,\beta$		$\alpha-1.5032\,\beta$
α_2	$\alpha+1.8173\,\beta$		$\alpha+2.2954\,\beta$
α_3	$\alpha+0.5453\,\beta$		$\alpha+0.3632\,\beta$
α_4	$\alpha-0.0032\,\beta$		$\alpha-0.0423\,\beta$
β_{12}		$0.3963\,\beta$	
β_{23}		$1.1581\,\beta$	
β_{34}		$1.0179\,\beta$	
β_{45}		$0.9720\,\beta$	

TABLE 5

EIGEN-VALUES, LINEAR COEFFICIENTS AND THE FIGURES FOR THE π–π^* TRANSITION OF *N*-(TRIMETHYLSILYL)-PYRROLE

	c_1	c_2	c_3	c_4	c_5	c_6
$E_1=\alpha+3.3675\,\beta$	0.0671	0.8219	0.3690	0.1542	0.1542	0.3690
$E_2=\alpha+1.2437\,\beta$	0.0574	0.3984	−0.1908	−0.6184	−0.6184	−0.1908
$E_3=\alpha+0.9036\,\beta$	0.0000	0.0000	0.6246	0.3315	−0.3315	−0.6246
$E_4=\alpha-0.9488\,\beta$	0.2607	0.3648	−0.5556	0.3011	0.3011	−0.5556
$E_5=\alpha-1.5547\,\beta$	0.0000	0.0000	0.3315	−0.6246	0.6246	−0.3315
$E_6=\alpha-1.5774\,\beta$	0.9612	−0.1800	0.1367	−0.0556	−0.0556	0.1367
Δm			$1.8524\,\beta$			

TABLE 6

COMPARISON OF CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS OF PYRROLE, *N*-TERT-BUTYLPYRROLE AND *N*-(TRIMETHYLSILYL)PYRROLE

Compound	μ_σ (D)	μ_π (D)	$\mu_{\sigma\pi}$ (D)	$\mu_{\text{exp.}}$ (D)	Deviation (D)
Pyrrole	0.1036	2.0861	2.1897	1.83[11]	−0.3597
N-tert-Butylpyrrole	0.1034	2.0861	2.1895	1.835[2]	−0.3545
N-(Trimethylsilyl)pyrrole	0.7493	1.4360	2.1853	2.224[2]	+0.0387

chromic shift (216 nm/217 nm)[1] in the ultraviolet spectra. Calculated and experimental figures for dipole moments are shown in Table 6.

Since the extended Hückel method cannot distinguish the π-system of *N*-tert-butylpyrrole from the π-system of pyrrole, for the μ_π dipole moment of *N*-tert-butylpyrrole the figure calculated for pyrrole was taken. That the effect of the tertiary butyl group and the effect of hydrogen bonded to the nitrogen are nearly the same is proved by the fact that pyrrole and *N*-tert-butyl-pyrrole have the same μ_σ dipole moments. There is good agreement between the experimental dipole moments, and the ultraviolet absorption maxima, of the two compounds[1,2]. The resulting dipole moments calculated for the three compounds are the same; deviation from experimental values is smallest in the case of the silicon derivative. The highest figure for the dipole moment of *N*-(trimethylsilyl)pyrrole can be accounted for by a higher μ_σ-, and a lower μ_π-dipole moment with respect to pyrrole.

Figure 3 shows that the silicon–nitrogen bond is defined by a π-bond order of 0.156. This is in good agreement with the value of 0.18 obtained by Kriegsmann[12] for hexamethyldisilazane.

The extended approximation method of Hückel uses coulomb- and resonance-integrals that disregard electronic interactions and in some cases, therefore, there are important deviations from experimental results. In a following communication our calculations according to the Pariser–Parr–Pople (more exactly, according to the SCF-LCAO-MO-PPP-CI) method will be discussed. This method yields better results for structures of molecules because it takes the effects of all the atoms into account in the calculation of the integrals. With the PPP method, the results obtained are in better agreement with experimental data.

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