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Commentationes

Theoretical Studies in the Chemistry and Physics of Heterocycles

I. The π-Electron System and U.V. Spectrum of Pyrrole

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LCAO–SCF calculations with four different sets of parameters are given for the π-electron structure of pyrrole. The aim was mainly to discuss whether such a kind of calculations could account for the molecular properties, or the σ system ought to be explicitly included. The effects of different values for the integrals were discussed by comparing final results, concerning both the ground state and the excited states. A good agreement with experimental data was obtained. The usual limited configuration mixing on our SCF results, leading to a poor agreement for the energies as well as to a lack of qualitative sequence of intensities, does not allow a clear interpretation of the U.V. spectrum.

La méthode LCAO–SCF–MO est appliquée a l'étude de la structure π électronique du pyrrole en utilisant quatre séries différentes de parametres. On discute en quelle mesure cette sorte de calculs peut expliquer les propriétés moleculaires, ou bien s'il faut tenir compte du systeme σ. Notre attention est particulierement dévouée à l'effect du choix de différentes valeurs des intégrales sur les résultats des calculs, à l'égard des propriétés soit de l'état fondamental comme des états excités. On obtient un très bon accord avec les données experimentales. On conclue enfin qu'une intéraction de configuration limitée ne porte pas à une interpretation sûre du spectre U.V., ni pour les énergies d'excitation ni pour la séquence des intensités.

Einige LCAO-SCF-Rechnungen werden für Pyrrol mit verschiedenen Parametersätzen durchgeführt, um zu klären, ob die Betrachtung der π-Elektronen allein eine befriedigende Beschreibung der molekularen Eigenschaften erlaubt oder auch die σ-Elektronen explizit betrachtet werden müssen. Der Einfluß verschiedener Integralwerte auf die Endergebnisse wird für den Grundzustand und die angeregten Zustände diskutiert. Die Übereinstimmung mit den experimentellen Ergebnissen ist gut. Die gewöhnliche begrenzte Konfigurationswechselwirkung gibt keine klare Interpretation der UV-Banden, weil für die berechneten Energien und Intensitäten die Übereinstimmung mit den experimentellen Werten nicht so gut ist.

I. Introduction

The present paper is the first of a series devoted to the application of quantum theoretical calculations to the chemistry and physics of five-membered heterocycles and their derivatives. We shall consider here the π-electrons of pyrrole. Our purpose is both to make a new study of pyrrole and to clarify certain aspects of the current methods for treating π-electrons. The latter problem is particularly important as a preliminary step to the inclusion of σ electrons, for, if a complete calculation based on strong σ-π separation is to be carried out, the procedure for calculating the π contribution must be chosen on the basis of a very careful discussion.

Most calculations so far carried out on pyrrole consist in SCF procedures often followed by some configuration mixing. In particular, BROWN and HEFFERNAN [2] and DAHL and HANSEN [5] took into account the ground-state and the single-excited configurations to obtain a satisfactory general agreement between the theoretical predictions and the experimental data.

However, Ref. [2] failed to give a reasonable prediction for the second excited singlet, even if the authors considered two different ways (calculations A and B) of introducing penetration integrals (see Fig. 1). They saw the origin of this deviation in the very nature of the SCF–CI method, for disagreements of the same kind had been found with other molecules, e.g. with pyridine [13].

On the basis of this consideration the authors of Ref. [5] repeated BROWN and HEFFERNAN's calculations by modifying the Coulomb integrals according to MATAGA and NISHIMOTO's equation [12] which had been used succesfully in the azine series.

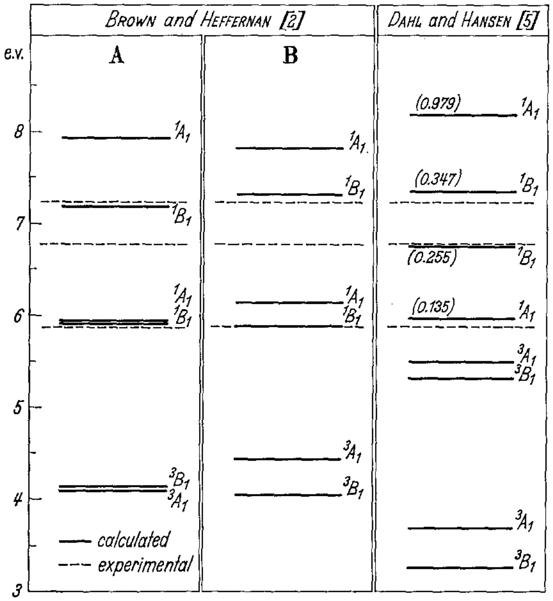

Fig. 1

The results led to a very good agreement with the observed spectrum, and thus gave the impression that there existed a close analogy between the π systems of pyrrole and of the azines. However, the effect of the change of the Coulomb integral values on the energy calculated for the second electronic transition may depend on the values of the penetration integrals: if so, the analogy in question must be regarded as purely incidental. This indicates that the role of penetration integrals in an SCF calculation on pyrrole should be the object of further studies: in fact, it suggests that, by choosing those integrals conveniently, and possibly without introducing any configuration mixing, one could find at the same time a predicted spectrum as good as that of Ref. [5], and significant differences in the description of the ground state. The following considerations give further support to this view. Both B. and H. (proc. A) and D. and H. evaluated theoretically the penetration integrals using Slater atomic orbitals. We think that this procedure introduces some inconsistency in the method; for the other integrals were evaluated empirically, and they were often quite different from their theoretical values. Those different criteria for evaluating different kinds of integrals are in a sense equivalent to using two different atomic orbital bases: a basis of Slater orbitals for penetration integrals, and a basis not explicitly defined for the other integrals. This would be a minor detail if the penetration integrals involved only neutral atoms, for then they would be small, and possible differences arising from different criteria for evaluating them would have little effect on the final results. But, since the nitrogen atom is doubly ionized in the core of pyrrole, we have to evaluate also the penetration integrals on a charged atom. Now the GOEPPERT-MAYER and SKLAR treatment of core energies [*6*] leads to the equation:

$$(\overset{+}{\mathrm{N}}:\mathrm{CC}) = (\mathrm{N}:\mathrm{CC}) + (\mathrm{NN}/\mathrm{CC}) \;;$$

and, as both values of $(\mathrm{N}:\mathrm{CC})_{th}$ and $(\mathrm{N}:\mathrm{CC})_{emp.}$ are very small, it follows that the differences between the values of $(\overset{+}{\mathrm{N}}:\mathrm{CC})_{th},$ and $(\overset{+}{\mathrm{N}}:\mathrm{CC})_{emp.}$ are essentially the differences between the theoretical and empirical values of the repulsion integrals. For the pair of neighbouring C–N atoms in pyrrole this difference amounts to 2 eV and 4 eV, if we calculate the repulsion integral by the Pariser and Parr's equation or the Mataga and Nishimoto's equation, respectively. As empirical values of the repulsion integrals are used in the kind of calculation, we conclude that the penetration integrals in Ref. [*2*] (proc. A) and Ref. [*5*] are overstimated by a margin that is not negligible: this fact should affect the final results, both as regards the ground state properties, and as regards the U.V. spectrum.

In an attempt to clarify the points just mentioned, we have tried to set up an SCF method, which would be consistent with the above remarks concerning the choice of the integrals and, at the same time, would predict correctly the U.V. spectrum of pyrrole. We intend to report here on the results obtained and the conclusions reached.

II. Method of Calculation

As has been said, we treated by an SCF procedure the π-electrons of pyrrole in the field of the nuclei and of the other electrons. The atomic orbitals χ_p were not defined explicitly, for we assumed only that they were consistent with the empirical values assigned to all the integrals of ROOTHAAN's theory [*22*], in the P–P–P (zero differential overlap) and GOEPPERT-MAYER and SKLAR [*6, 16, 17, 19*] approximations. In their most complete form these approximations express the core integral α_p as:

$$\alpha_p = W_p - \sum_{q \neq p} [D_q\,(pp/qq) + (q:pp)] - \sum_r (r:pp)$$

and the energy matrix elements as:

$$H_{pp} = W_p - \sum_{q \neq p} (D_q - q_q)\,(pp/qq) - \sum_{q \neq p} (q:pp) - \sum_r (r:pp) + \tfrac{1}{2}\,q_p\,(pp/pp)$$

$$H_{pq} = \beta_{pq} - \tfrac{1}{2}\,l_{pq}\,(pp/qq)\,.$$

Where D_q is the number of the positive charges on the atom q in the core ($D_q = 1$ for carbon atoms while $D_q = 2$ for nitrogen in pyrrole) and the other symbols have the usual meanings.

III. Empirical Evaluation of the Integrals

We suppose [*10, 15*] that W_p and (pp/pp) depend linearly on the effective charge Z_p^*

$$W_p = m_p Z_p^*$$

$$(pp/pp) = K_P Z_p^* \, .$$

For the effective nuclear charge we have:

$$Z_p^* = Z_p \left[1 + \varepsilon_p (N_p - q_p)\right]$$

with Z_p from Slater's rule: N_p is the number of the electrons in the $2pz$ orbital of the atom p and so $(N_p - q_p)$ represents the formal charge on the atom in the molecule.

At each iteration the M.O. coefficients, and, therefore, the electronic populations q_p, are changed: a change in the values of Z_p, W_p and (pp/pp) occurs in consequence. The constants ε_p for nitrogen and carbon are:

$$\varepsilon_N = 0.0898 \qquad\qquad \varepsilon_C = 0.1077 \, .$$

We evaluated the two-centre repulsion integrals (pp/qq) both with the P–P and M–N methods; these integrals depend on the effective charge and so they were recalculated at each iteration.

The penetration integrals were obtained by parabolic interpolation between the values at the origin and at 2.80 and 3.70 Å:

$$r_{pq} = 0\ \text{Å} \qquad\qquad (q{:}pp) = A$$

$$r_{pq} = 2.80, \quad 3.70\ \text{Å} \qquad\qquad (q{:}pp) = 0$$

where A is either the electron affinity if p and q are alike or is the result of multiplying the electron affinity of atom q by the ratio Z_p/Z_q if p and q are atoms of different species. Owing to the rather low values of the integrals in question we did not change them with the effective charge during the calculations.

The bond integrals, β_{CC}, were evaluated by adapting the value proposed by Pariser and Parr ($\beta_{CC} = 2.39$ eV at $r_{CC} = 1.397$ Å) to the bond length [*9*].

On the basis of the experimental results of Bak and coll. [*1*] for the structure of pyrrole, we gave these integrals the values:

$$\beta_{C_2C_3} = -\,2.67\ \text{eV} \qquad\qquad \beta_{C_3C_4} = -\,2.08\ \text{eV} \, .$$

The β_{CN} value was chosen so as to reproduce the energy of the first singlet electronic transition.

The bond integrals between non-neighbouring atoms were also introduced [*9*].

With the method just described we carried out four calculations (which will be called A, B, C, D) with the aim of analysing by comparison the effect of the different choises of the integrals on the final results.

In Tab. 1 we report the values of the parameters we used in the different calculations.

Table 1

	A	B	C	D
$K_C = K_N$	3.025	3.294	3.025	3.294
(pp/qq)	Pariser Parr		Mataga Nishimoto	
β_{CN}	−3.00	−2.65	−2.50	−2.10
β^*_{CN}	−3.25	−2.80	−2.50	−2.10
m_p	$m_C = 3.4339$		$m_N = 6.8612$	

β^*_{CN}: Values of the bond integrals chosen so as to reproduce the energy of the first singlet electronic transition after configuration mixing (see Fig. 1).

IV. Results

We report in Tab. 2 the final values of the effective nuclear charges Z^*_p, of the valence-state energies W_p, of the core integrals α_p and of the one-centre and two-centre Coulomb integrals. At the bottom of Tab. 2 we report also the fixed values of

$$P_{(p)} = \sum_{q \neq p} (q:pp) + \sum_{r} (r:pp)$$

entering the core integrals α_p. The usual numbering of the pyrrole ring is used, the nitrogen atom being number 1. Tab. 3 gives the charge populations and the π-dipole moments μ_π and Tab. 4 gives the bond orders l_{pq} and the calculated and

Table 2

	A	B	C	D
Z^*_1	3.9921	3.9866	3.9583	3.9500
Z^*_2	3.2230	3.2213	3.2321	3.2320
Z^*_3	3.2309	3.2353	3.2386	3.2428
W_1	−27.3911	−27.3536	−27.1592	−27.1025
W_2	−11.0676	−11.0614	−11.0987	−11.0985
W_3	−11.0945	−11.1098	−11.1209	−11.1353
α_1	−54.4561	−55.1706	−46.3924	−47.0255
α_2	−45.1491	−46.1773	−35.3414	−36.2622
α_3	−42.9088	−43.6835	−33.5904	−34.4304
(11/11)	12.0787	13.1161	11.9731	13.0115
(22/22)	9.7486	10.5980	9.7766	10.6465
(33/33)	9.7723	10.6444	9.7962	10.6818
(11/22)	7.4675	7.7661	5.3185	5.5370
(11/33)	5.8201	5.8977	4.0534	4.1798
(22/33)	7.0831	7.3598	5.0655	5.2909
(22/44)	5.6358	5.7009	3.8606	3.9901
(22/55)	5.6448	5.7097	3.8663	3.9954
(33/44)	6.9857	7.2485	4.9667	5.1846
$P_{(1)}$	0.4894			
$P_{(2)}$	0.8133			
$P_{(3)}$	0.4699			

Table 3

	Brown A	Brown B	Dahl and Hansen	A	B	C	D	exp
q_1	1.658	1.700	1.612	1.737	1.753	1.833	1.857	
q_2	1.151	1.076	1.167	1.077	1.082	1.051	1.051	
q_3	1.019	1.074	1.028	1.054	1.042	1.032	1.020	
μ_π	1.59	2.12	1.84	1.60	1.48	1.03	0.81	1.80

Table 4

	Dahl-Hansen		A		B		exp
p—q	l_{pq}	r_{pq}	l_{pq}	r_{pq}	l_{pq}	r_{pq}	r_{pq}
1—2	.4750	1.337	.4119	1.369	.3966	1.372	1.383
2—3	.7950	1.377	.8273	1.368	.8411	1.366	1.371
3—4	.5240	1.422	.4988	1.429	.4771	1.433	1.429

Table 5

	A		B		C		D		
symmetry	energy eV	f	energy eV	f	energy eV	f	energy eV	f	exp eV
$^1B_1$	5.869	0.36	5.876	0.34	5.899	0.33	5.898	0.31	5.87
$^1A_1$	6.776	0.50	6.799	0.53	6.988	0.52	7.056	0.53	6.77
$^1A_1$	6.935	0.42	7.176	0.44	7.205	0.45	7.389	0.47	7.22
$^1B_1$	7.306	0.15	7.452	0.14	8.216	0.10	8.411	0.09	
$^3B_1$	4.276		4.000		3.261		2.939		4.35
$^3A_1$	5.375		5.077		5.006		4.868		

experimental bond lengths r_{pq}. The energy differences between the lowest excited triplet and singlet states and the ground state are compared with the experimental values of the U.V. spectra on Tab. 5, where we report also the symmetry assignment and the oscillator strength f calculated following Mulliken's method.

V. Discussion

Tab. 3 – 5 illustrate the effect of different choices of penetration and Coulomb integrals, for the differences in the other parameters (e.g. the β_{CN} values) affect them much less. In the light of this remark, we discuss here the results obtained for the ground state, charges and dipole moment, and the transition energies. We shall also discuss the effects of some configuration mixing.

The ground state of pyrrole

The description arrived at for the ground state of pyrrole by the method under consideration is very sensitive to the values chosen for the penetration integrals. Larger values of the latter appear to enhance the delocalisation of the nitrogen π-electrons and the difference in the electron populations between the α and β

positions. This can be seen by comparing calculations using the theoretical values of the penetration integrals (Ref. [*2*] proc. A, Ref. [*5*]) and our calculations, where the integrals in question have lower values. For instance, in the latter case, the difference in the electron populations of the α and β positions are smaller than those of Ref. [*2*] and [*5*].

Some indications that our description of the ground state of pyrrole is possibly the more realistic can be found in the following considerations. If one accepts the current interpretation of electron populations as reactivity indices of a molecule in a neutral environment [*21*], our results appear to agree quite well with chemical facts. In fact, according to J. Ridd [*21*], while the electrophilic attack occurs mainly at the α position, the α and β positions do not differ greatly in reactivity. Furthermore, assuming that the so-called bond orders can be related empirically to bond lengths using, for instance, Julg's formula [*8*]:

$$r_{pq} = \sqrt{\frac{3.25}{\frac{1}{2}(Z_p + Z_q)}}\,(1.52 - 0.19\, l_{pq})$$

we can check the consistency of the results obtained for the ground state with the experimental geometry of the molecule. Tab. 4 shows that our A and B calculations give a close agreement, while Ref. [*5*] leads to a length of the C–N bond much smaller than that known experimentally (1.337 and 1.383 Å, respectively); and this suggests that the delocalisation of the electron pair of the nitrogen atom and the electron population on the α carbon atom are probably too large. (This seems to be a common feature of results obtained using theoretical values for penetration integrals on a charged atom).

Finally, the electric dipole moments obtained with procedures A and B, which also give the best predictions of the U. V. spectrum, have values in close agreement with experiment. Even the fact that they are somewhat lower is reasonable, because probably a slight σ moment in the same direction should be added to them.

The ultraviolet spectrum

The available experimental data are reported in Tab. 5, where, besides the singlet-singlet transitions [*14, 18, 20*], a transition at 4.35 eV corresponding to a very weak band ($\varepsilon < 0.1$) is reported: owing to its sensitivity to oxygen it should be a singlet-triplet one* [*11*].

In our calculations it can be attributed to the first singlet-triplet transition. As concerns the singlet, all our results show a close agreement with the experimental data, even if some uncertainty appears in the assignment of the 7.22 eV band. For this band, we are not satisfied with the assignment $^1B_1$ suggested by calculation A, for the oscillator strength calculated for it appears to be lower than that of the first band, which conflicts with the intensity sequence generally accepted for the U.V. spectrum of pyrrole. On the other hand, calculation A leads to a close agreement for the triplet state energy.

Effect of configuration mixing

As can be seen, we have succeeded in obtaining a satisfactory description both of the ground state and of the U.V. spectrum of pyrrole without introducing any

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* The authors are grateful to Prof. S. F. Mason for the permission to report this impublished datum.

configuration mixing; however, in order to understand better the role played by Coulomb and penetration integrals in determining the pattern of the spectrum and to discuss the effects of some configuration interaction, we have allowed the excited state configurations to mix, as was done in Ref. [2] and [5], adjusting the β_{CN} so as to reproduce the first experimental transition.

The results are shown in Fig. 2 under asterisks. [Fig. 2 also shows the results already reported in Tab. 5 (non-asterisk). The dotted lines given in Fig. 2 represent experimental data.] It is evident that the procedure involving configuration mixing, leads to a poor agreement between theoretical and experimental energies and to an unrealistic intensity sequence; therefore, it does not allow a reasonable interpretation of the spectrum of pyrrole.

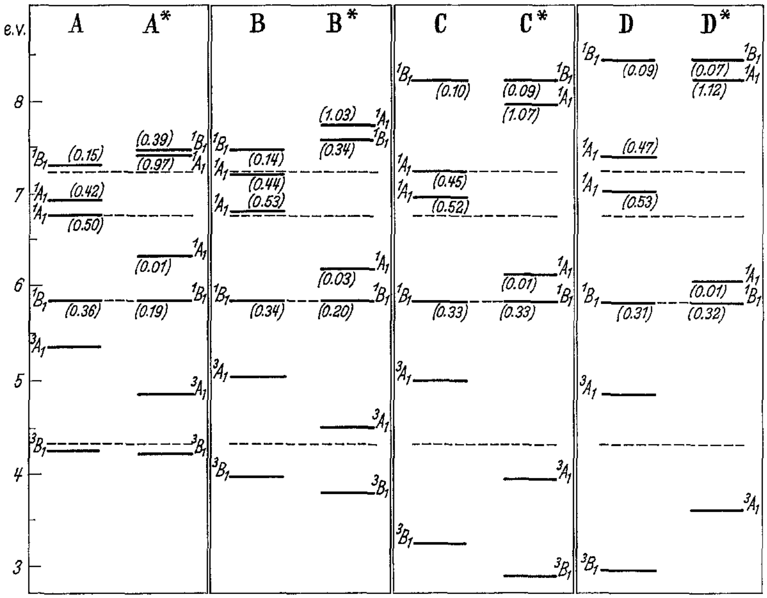

Fig. 2

That the M–N electronic repulsion integrals do not suceeded any more than the P–P integrals in providing a better value for the second singlet energy is clearly seen by comparing B* and D* calculations; furthermore, by comparing D* and B* respectively with Ref. [5] and Ref. [2] (proc. A) (see Fig. 1), we deduce that good results are obtained with M–N repulsion integrals only if theoretical penetration integrals are used.

VI. Conclusions

The most important conclusions reached in the present work can be summarized as follows:

1. In semi-empirical calculations also the penetration integrals should be given empirical values. The latter appear to be lower than the theoretical ones, just as in the case of the other integrals; the differences are important only when the corresponding penetration integrals involve charged atoms. The calculated ground

state properties are very sensitive to these integrals; in particular, the delocalisation of the electron pair of the nitrogen atom is too high if theoretical values are used. As regards the role of penetration integrals in determining the expected excited-state energies, a comparison of different calculations for pyrrole suggests that those on neutral atoms can be either neglected or evaluated empirically; those on charged atoms should be evaluated empirically.

2. Our results are in fairly good agreement with the ground state experimental data and with the spectrum of pyrrole provided (a) no configuration mixing is introduced and (b) very low empirical penetration integrals and P–P type electronic repulsion integrals (our procedures A and B) are introduced.

3. The electronic repulsion integrals according to M–N are not more convenient than those according to P–P, either in an SCF or in an SCF–CI method. However, as concerns the spectrum of pyrrole a close agreement with experiment is obtained by using M–N repulsion integrals provided theoretical values of penetration integrals are used (Ref. [*5*]).

4. Using different sets of parameters we have shown that, at least for pyrrole, results are in better agreement with experiment if a SCF calculation is carried out without any configuration mixing rather than with the usual limited configuration mixing.

We have thus seen that a standard π-calculation on pyrrole leads to results well accounting for experiment and even better results could be obtained with an even more careful choice of parameters. As far as the properties of pyrrole here examined are concerned, it does not seems to be necessary to introduce explicitly the σ-electrons. There are two possible explanations for this: (a) that the empirical choice of the integrals has taken into account at least part of the σ effects; (b) that the effects are in fact small even as regards the ground state. The latter alternative is supported by the fact that the μ_σ dipole moment of pyrrole, calculated by various additive rules, has a very low value (0.2 – 0.3 D). Therefore, a choice between the two alternatives, and a detailed analysis of them, should result out of a study of other heterocycles, like furan and tiophene. These compounds appear to have high μ_σ dipole moments: consequently, if alternative (b) were correct, one should expect their ground states to be described rather poorly by the procedure used in this paper, especially as regards the significance of charge distributions.

We shall discuss the above question in a subsequent paper.

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