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A SELF CONSISTENT FIELD MOLECULAR ORBITAL TREATMENT OF PYRROLE AND PYRROLE ANION INCLUDING ALL VALENCE ELECTRONS

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Abstract—The electronic structures of pyrrole and pyrrole anion have been investigated using the Pople–Segal Complete Neglect of Differential overlap self consistent field MO theory, including all valence electrons. For pyrrole the charge distribution and energy levels have been compared with those obtained from the *ab initio* calculations of Clementi *et al.* The latter calculation appears to give an excessive amount of charge migration from the H atoms, and the charge distribution obtained by the semi empirical SCF calculation is probably more realistic. In general there is reasonable agreement between the orbital energies calculated by the two methods, energy level differences being particularly well produced. For pyrrole anion comparison of charge distribution, with that obtained using Extended Hückel Theory indicates that the latter is likely to be seriously in error when used in calculations on polar molecules.

INTRODUCTION

ALTHOUGH the pi electronic structure of pyrrole (Fig. 1) has been extensively discussed in terms of simple Hückel theory$^{1-4}$ and the more sophisticated Pariser–Parr–Pople self consistent field MO method,$^{5-9}$ there have been few attempts to study the sigma electronic structure of this molecule.

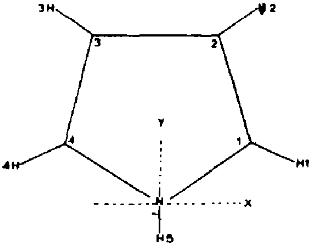


FIG. 1 Numbering and co-ordinate system for pyrrole.

The polarized sigma core will obviously affect the pi electron distribution and *vice-versa* and hence the calculations which have been carried out on the pi electronic structure of pyrrole neglecting this factor must be treated with caution. A further criticism which may be levelled at previous MO treatments of pyrrole is the neglect of non nearest neighbour β's, which for a small ring compound such as pyrrole is quite a serious approximation.^{10} In the light of this discussion a self consistent field MO calculation, including all valence electrons, on pyrrole is clearly worthwhile.

In a recent series of papers Pople *et al.*[11–13] have formulated a new approximate method for calculating self consistent molecular orbitals, including all valence electrons. The so called Complete Neglect of Differential overlap Method II.[13] The theory has been applied to numerous small molecules with spectacular success in calculating dipole moments, charge distributions and energy[12, 13] differences. It is of considerable interest therefore to apply this theory to a larger molecule such as pyrrole to calculate both sigma and pi electron distributions and total dipole moments. A related molecule also of interest is the pyrrole anion, formed from pyrrole by removal of a proton from the N atom.

Since this work was initiated two papers have appeared on the electronic structure of pyrrole[14, 15] and pyrrole[15] anion, including all valence electrons, which have changed the emphasis of this work. The timely appearance of the *ab initio* calculations on pyrrole by Clementi *et al.*,[14] is most welcome since it provides a yardstick for comparison with semi empirical calculations of the type presented here. The extended Hückel calculations of Adam *et al.*[15] are also of interest, particularly for the charged pyrrole anion, since they represent a stage lower in order of sophistication than the calculations presented here and pose some interesting questions. For example, the sigma and pi charge distributions are predicted to be essentially the same in pyrrole and pyrrole anion, a result which would seem to be highly unlikely. The emphasis throughout this paper will hence be on comparing and contrasting the results obtained here with those obtained by the more sophisticated *but* ab initio calculations of Clementi and the extended Hückel calculations of Adam *et al.*

Method of calculation

The calculations have been carried out using the Pople-Segal Complete-Neglect of Differential overlap Method II.[13] The theory has been applied to numerous small molecules with a good deal of success and it is therefore of considerable interest to apply this method to larger molecules such as pyrrole (25 orbitals). The elements of the F matrix are given by Eqs 1 and 2 (notation Ref. 13).

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB} \tag{1}$$

where $U_{\mu\mu} = -I_\mu - (Z_A - 1)\gamma_{AA}$

$$F_{\mu\nu} = \beta - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{2}$$

Eq. (1) neglects the penetration terms, the equations are formally similar to those used in the highly successful Pariser–Parr[16]–Pople[17] SCF theory of pi electronic structure of molecules.

As in the latter theory, the main problem is the estimation of the core and repulsion integrals and the β's which occur in the off diagonal elements of the F matrix. Pople *et al.* have estimated the one centre core integrals from the average of valence state ionization potential and electron affinities,[13] however valence state ionization potentials are in general more accurately known than electron affinities, so we have approximated the core integrals as the average of valence state ionization potentials in the manner described by Sichel and Whitehead.[18]

In their original paper Pople and Segal[12] assigned to γ_{AA} the analytic value of the electrostatic repulsion energy of two electrons in a Slater S orbital. This does not allow for correlation energy, and hence we prefer to use the method due to Pariser,[19] which has been applied so successfully in the PPP SCF method, of evaluating the γ_{AA} from Eq. (3).

$$\gamma_{AA} = I_{AA} - A_{AA} \tag{3}$$

where I_{AA} is the valence state ionization potential of atom A

A_{AA} is the valence state electron affinity of atom A.

Whitehead[18] has investigated this method in detail and the parameters used here are taken from his paper.

The two centre repulsion integrals γ_{AB} were calculated from the corresponding one centre repulsion integrals using the refined Mataga procedure[20] Eq. (4).

$$\gamma_{AB} = \frac{14{\cdot}397}{(a_{AB}^2 + r_{AB}^2)^{\frac{1}{2}}} \text{ where } a_{AB} = \frac{(2 \times 14{\cdot}397)}{\gamma_{AA} + \gamma_{BB}} \tag{4}$$

The first term in the off diagonal elements of the F matrix (β's) were made proportional to overlap integrals in the original Pople papers,[12,13] in order to maintain the invariance to the transformation of atomic orbital basis functions. The required overlap integrals were calculated using Slater orbitals and orbital exponents calculated using Slater's rules,[21] except for the hydrogen 1s orbital (Z effective taken as 1·2). However Burns[22] has recently shown that Slater orbitals defined using Slater's rules, are not good approximations to SCF orbitals at distances from the nuclei appropriate for bonding and has devised a modified set of Slater's rules. The orbitals defined in this manner yield overlap integrals which approximate those calculated using SCF orbitals, in particular the slow tailing off of the latter is reproduced. In general overlaps calculated in this manner are larger than those obtained using Slater's rules. In crude pictorial terms $\beta_{\mu\nu}$ represents the energy of the overlap density $S_{\mu\nu}$ in the average field of the two cores μ and ν. The direct proportionality of β to overlap integral is therefore quite a drastic approximation. We prefer instead to use another empirical relationship Eq. (3) due to Mulliken, Wolfsberg and Helmholtz.[23]

$$\beta_{\mu\nu} = K \frac{(I_{\mu\mu} + I_{\nu\nu})}{2} S_{\mu\nu} \tag{3}$$

Where $I_{\mu\mu}$ and $I_{\nu\nu}$ are appropriate valence state ionization potentials of atoms μ and ν, K is a constant and $S_{\mu\nu}$ is the overlap integral between atoms μ and ν. Two centre core integrals calculated from (3) with $K = 1$ are close in magnitude on the average to those obtained using Pople's recipe and weight the β's involving S orbitals on carbon and nitrogen. The integrals involving only P orbitals are essentially the same as those found necessary by Clark and Ragle[24] to give a good account of the pi electronic structure of benzene in the Pople–Segal framework. The use of Eq. (3) is open to criticism from the purists on the grounds that it is not invariant to a transformation of atomic orbital basis functions.[11] However, preliminary calculations showed that this effect is negligible compared with the total energy calculated for the molecule, and the latter should be reliable to the second place of decimals. This is in line with calculations carried out using extended Hückel theory.[25,26]

Table 1 lists the parameters employed in these calculations. Bond lengths and bond angles were taken from Ref. 27 for pyrrole. For the pyrrole anion, the geometry was assumed to that of pyrrole with the appropriate H atom removed.

TABLE 1. ONE CENTRE INTEGRALS

Orbital	Atom	Z effective	$-I_{\mu\mu}$	$-U_{\mu\mu}$	$\gamma_{\mu\mu}$
1s	H	1·2	13·60	13·60	12·85
2s	C	3·150	20·07	50·69	10·207
2p	C	2·800	10·910	41·53	
2s	N	3·750	25·89	70·09	11·05
2p	N	3·300	13·65	57·85	

The calculations were carried out on the University of Newcastle's KDF9 computer using a program kindly supplied by Drs. P. G. Perkins and D. H. Wall. Limitations of storage capacity (16K) dictated that the initial H matrices should be calculated previously and used as input data, together with atomic co-ordinates gammas and core charges. 25 iterations were sufficient to obtain density matrix elements self consistent to seven decimal places. Overlap integrals were calculated from a compilation of master formulae kindly supplied by Dr. P. G. Perkins.

RESULTS AND DISCUSSION

A. *Charge distribution and dipole moment of pyrrole*

Tables 2 and 3 show the distribution of charge between the atomic orbitals of

TABLE 2. THE DISTRIBUTION OF CHARGE BETWEEN THE ATOMIC ORBITALS IN PYRROLE (THE Z AXIS IS $\perp$ TO THE MOLECULAR PLANE, THE CO-ORDINATE AXES IN REF. 14 HAVE BEEN TRANSFORMED TO CORRESPOND WITH THE DEFINITION USED IN FIG. 1)

Atom and orbital		This work	Ref. 14
$H_1(H_4)$	1s	0·9832	0·7962
$H_2(H_3)$	1s	0·9726	0·8084
H_5		0·8449	0·6610
$C_1(C_4)$	2s	1·0059	1·0469
	$2p_x$	0·8624	1·0217
	$2p_y$	0·9694	0·9624
	$2p_z$	1·0869	1·0752
$C_2(C_3)$	2s	1·0096	1·0560
	$2p_x$	0·9943	1·0310
	$2p_y$	0·9987	1·0741
	$2p_z$	1·0854	1·0953
N	2s	1·2032	1·3709
	$2p_x$	1·2416	1·1440
	$2p_y$	1·1181	1·2364
	$2p_z$	1·6553	1·6589

pyrrole and the total σ and π charge distributions. For comparison the results obtained by Clementi[14] and Adam[15] are included.

TABLE 3. TOTAL SIGMA, PI, ELECTRON AND CHARGE (δ) DISTRIBUTION IN PYRROLE

Atom		Electron population			δ (charge)		
		This work	Ref. 14	Ref. 15	This work	Ref. 14	Ref. 15
$H_1(H_4)$		0·9832	0·7962	—	+0·01677	+0·2038	—
$H_2(H_3)$		0·9726	0·8084	—	+0·02738	+0·1916	—
H_5		0·8449	0·6610	—	+0·15513	+0·3390	—
$C_1(C_4)$	σ	2·8377	3·0302	2·8200	+0·1623	−0·0302	+0·1800
	π	1·0848	1·0752	1·0800	−0·0848	−0·0752	−0·0800
$C_2(C_3)$	σ	3·0026	3·1602	3·0300	−0·0026	−0·1602	−0·0300
	π	1·0854	1·0953	1·1300	−0·0854	−0·0953	−0·1130
N	σ	3·5629	3·7448	—	−0·5629	−0·7448	—
	π	1·6553	1·6589	—	+0·4447	+0·4411	—

The most striking feature of Tables 2 and 3 is the large amount of charge migration from the H atoms given by Clementi's[14] calculation. To put these charge migrations in proper perspective we may draw a comparison with the charge migration from hydrogen in a highly polar molecule such as HF as computed by Ransil.[28] In this case the charge on hydrogen was calculated to be +0·1024. The charge migrations from hydrogen in Clementi's calculation are therefore almost certainly exaggerated, and those calculated by the Pople–Segal method are probably a much better estimate of the charge distribution as far as the hydrogens are concerned. The Pople–Segal calculation predicts that C_1 and C_4 are sigma electron donors whilst C_2 and C_3 are almost neutral. Approximately the same result is predicted by the extended Hückel calculation. All four C atoms are predicted to be sigma electron acceptors in Clementi's calculation and for the C atoms adjacent to nitrogen this would seem to be an unrealistic result. The order of magnitude of the π electron distributions are remarkably similar for all three methods of calculation. A point of interest here is that the Pople–Segal calculation gives essentially the same pi electron density for $C_1(C_4)$ and $C_2(C_3)$ whereas the other calculations give a much higher electron density at $C_2(C_3)$ than at $C_1(C_4)$. PPP SCF[5–9] and refined ω technique calculations[29] on the pi electronic structure of pyrrole reverses the latter order, the calculation reported here is midway between the two extremes.

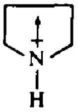
The overall charge distribution in a molecule is reflected in some measure by the total dipole moment. The two major contributions to the dipole moment of pyrrole are from:

(a) The net atomic charge densities

(b) The atomic (sp) polarizations resulting from mixing of s and p orbitals on each atom.

This represents a rather crude approximation to the molecular dipole moment, nonetheless Pople has shown that the method gives useful results. As there are no lone pairs of electrons in pyrrole the atomic polarization term is expected to be small. For example the value calculated for this term in this work is 0·43 Debyes.

A positive dipole moment contribution is defined in the sense



The experimental dipole moment of pyrrole is 1·80 Debye,[30] so it is clear that the major contribution to the molecular dipole moment must arise from term (a) defined above. The calculated contributions from the latter term calculated from Clementi's charge distribution and that reported here are 0·25 Debye and 1·08 Debye respectively. The small contribution calculated using Clementi's charge distribution arises from the charge migration from the hydrogens and this would tend to confirm that the calculation overemphasizes this migration. The total calculated dipole moment in this work is 1·53 Debye which is in good agreement with the experimentally determined value.

B. *Charge distribution in pyrrole anion*

Table 4 lists the total sigma, pi, electron and charge (δ) distribution in pyrrole anion.

TABLE 4. TOTAL SIGMA, PI, ELECTRON AND CHARGE (δ) DISTRIBUTION IN PYRROLE ANION

Atom		Electron population		δ (charge)	
		This work	Ref. 15	This work	Ref. 15
$H_1(H_4)$		1·04905	—	−0·04905	—
$H_2(H_3)$		1·03704	—	−0·03704	—
$C_1(C_4)$	σ	2·8484	2·7900	+0·1516	+0·2100
	π	1·08626	1·0800	−0·08626	−0·0800
$C_2(C_3)$	σ	2·98733	3·0300	+0·01267	−0·0300
	π	1·19260	1·1300	−0·19260	−0·1300
N	σ	4·1566	—	−1·1566	—
	π	1·4423	—	+0·5577	—

The removal of the proton from pyrrole to form pyrrole anion has some interesting effects on the electron distribution. As expected most of the negative charge remains localized on nitrogen, the sigma charge distribution on the C atoms not being very different from that in pyrrole itself. The H atoms acquire a small amount of negative charge. The calculated sigma and pi charges on the C atoms is very similar for both calculations. However, comparison with the calculated pi electron distributions for pyrrole (Table 3) columns 5 and 7 reveals the deficiency of Extended Hückel theory.[15] Since the sigma and pi systems are orthogonal, the pi electron distribution according to the Hückel calculation is unaffected by the polarity of the sigma core. This is obviously unrealistic. For example, an electron in a $2p_z$ orbital on nitrogen in pyrrole will be moving in a lower potential than in pyrrole anion where the nitrogen carries a negative charge, and therefore the pi electron density on nitrogen should be larger in the former case. The extended Hückel calculation predicts that they should be the same. In the Pople–Segal calculation on the other hand, although the sigma and pi systems are orthogonal, the elements of the F matrix Eq. (1) depend on the *total charge* on each atom, and hence allowance is made for the polarity of the sigma system.

C. *Energy levels and total energies*

Fig. 2 shows the sigma orbital energies for the ground state of pyrrole and for comparison those of Ref. 14.

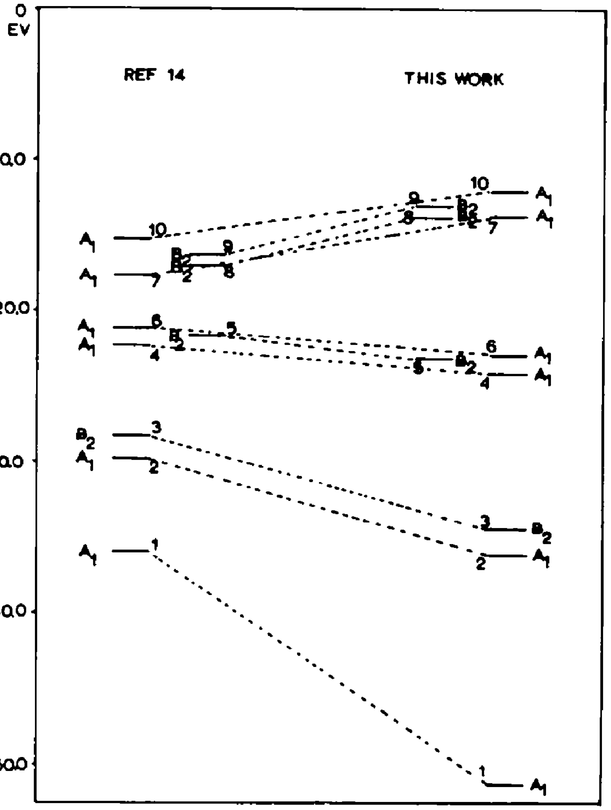


FIG. 2 Sigma orbital energies for the ground state of pyrrole. (For comparison those of Ref. 14 are also included).

The ordering of the energy levels is essentially the same for the two calculations. The energy levels calculated using the Pople–Segal method fall naturally into 4 groups. These are:

(i) The $A_1(\sigma)$ orbital at $-51{\cdot}687$ eV
(ii) The $A_1(\sigma)$ and $B_2(\sigma)$ orbitals centred around -35 eV
(iii) The $A_1(\sigma)$, $B_2(\sigma)$ and $A_1(\sigma)$ orbitals centred around -23 eV
(iv) The $A_1(\sigma)$, $B_2(\sigma)$, $B_2(\sigma)$ and $A_1(\sigma)$ orbitals centred around -13 eV.

This behaviour is also mirrored in the reference calculation,[14] and whilst the overall agreement between the energy levels is not particularly good for groups (i) and (ii), they are very reasonable for groups (iii) and (iv). Even more striking are the energy level differences within each group according to the two calculations. This is illustrated in Table 5. This reaffirms Pople's conclusions concerning the self consistent field MO calculation,[12] that the method is quite good for calculating energy level differences.

The ground state pi orbitals for pyrrole are given in Table 6.

TABLE 5. COMPARISON OF MOLECULAR ORBITAL ENERGY INTERVALS FOR THE SIGMA ORBITALS OF PYRROLE

Group	Interval	Δ (eV) This work	Δ (eV) Ref.
(ii)	$3B_2(\sigma)$-$2A_1(\sigma)$	+1·631	+1·660
(iii)	$6A_1(\sigma)$-$4A_1(\sigma)$	+1·178	+1·284
	$6A_1(\sigma)$-$5B_2(\sigma)$	+0·144	+0·521
(iv)	$10A_1(\sigma)$-$7A_1(\sigma)$	+1·599	1·932
	$10A_1(\sigma)$-$8B_2(\sigma)$	1·713	1·298
	$10A_1(\sigma)$-$9B_2(\sigma)$	0·906	0·697
	$9B_2(\sigma)$-$8B_2(\sigma)$	0·806	0·601

TABLE 6. GROUND STATE PI ORBITAL ENERGIES OF PYRROLE AND FOR COMPARISON THOSE OF REF. 14

Orbital Symmetry	Orbital energy	
	This work	Ref.
$B_1\pi$	−19·380	−17·178
$B_1\pi$	−11·063	−11·572
$A_2\pi$	−9·959	−10·556

The agreement is satisfactory. Applying Koopman's theorem the calculated ionization potentials is 9·959 eV. This compares favourably with the experimental value of 8·97 eV.[31]

The total energy calculated for pyrrole is −461·00 eV and that for pyrrole anion plus a proton −454·04 eV. The calculated energy for the process

$$\text{pyrrole (g)} \rightarrow \text{pyrrole anion (g)} + H^+(g)$$

is 6·96 eV.

This is almost certainly smaller than the experimental value a crude estimate of which can be made as collows. The energy of the process is given by Eq. (4)

$$\Delta\varepsilon = D(\text{N—H}) + I_H - A_N. \tag{4}$$

where D(N—H) is the bond dissociation energy of the N—H bond. I_H is the ionization potential of the H atom and A_N is the electron affinity of the orbital on nitrogen.

A reasonable estimate for D(N—H) is 3·87 eV[32] and I_H may be taken as 13·60 eV.

Applying Koopman's theorem the electron affinity of the orbital on nitrogen may be equated to the negative of the ionization potential of the sigma lone pair in pyrrole anion. This is calculated to be 6·21 eV and hence

$$\Delta\varepsilon = 11{\cdot}26\,\text{eV}.$$

CONCLUSIONS

The electronic structure of pyrrole and its anion have been studied by the Pople–Segal CNDO II SCF MO method. The method gives a reasonable account of the charge distribution and energy levels of the two molecules. The calculated charge distribution for pyrrole differs considerably from that obtained by Clementi mainly because of large charge migrations from hydrogen predicted by the latter. Comparison of charge contributions to the total dipole moment and with the results of full LCAO SCF calculations on HF would suggest that the charge distribution given by the Pople–Segal calculation is the more reasonable. A comparison of calculated charge distributions in the two molecules obtained in this work and those published using extended Hückel theory shows the deficiency of the latter in treating charged species.

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