The Electronic Structure of Heteroaromatic Molecules. Part 2.[1] Five-membered Rings

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Spin-coupled theory is applied to the π electrons of the heteroaromatic molecules furan, pyrrole, thiophene, and thiazole. As is the case for the six-membered rings considered in the companion paper, the electronic structure is described well in terms of localized but non-orthogonal orbitals. The characteristic stability of aromatic molecules results from the mode of spin coupling rather than from delocalized orbitals. The photoelectron spectra of these molecules are also considered briefly.

Spin-coupled calculations have shown that the π electrons in benzene, pyridine, pyridazine, pyrimidine, and pyrazine are much better described in terms of localized orbitals than they are by molecular orbital (MO) theory.[1,2] It is the mode of coupling the spins of the π electrons in these molecules that distinguishes them from non-aromatic systems.

It is widely accepted that the characteristic aromatic properties of five-membered heterocycles with six π electrons are linked to the delocalization of molecular orbitals. Based on our recent experience for six-membered rings, this appears to be somewhat unlikely. We present spin-coupled calculations for the heteroaromatic molecules pyrrole, furan, thiophene, and thiazole.

The spin-coupled description is a completely *ab initio* approach in which there are no preconceptions either to the form of the orbitals or of the type of spin couplings. The orbitals may turn out to be localized or delocalized according to whichever provides the lowest energy. In Part 1,[1] the results for the six-membered rings generally give substance to the ideas of classical valence bond (VB) theory, as long as one uses the fully optimized orbitals. In the cases treated here this is less obviously so. Some orbitals remain localized while others, particularly those stemming from the heteroatom, show a significant degree of delocalization. This description therefore deviates significantly from that of classical VB theory. A reasonably complete qualitative overview of the spin-coupled approach has been given in Part 1.

One of the great strengths of MO theory is the guidance it provides for the assignment of photoelectron spectra by means of Koopmans' theorem. Here we use the spin-coupled description to examine simple valence bond estimates of the ionization potentials. We show that the results from this procedure are at least as good for the lowest potentials as those derived from Koopmans' theorem, while the higher ones are considerably more reliable.

Calculations

The spin-coupled calculations in the present work were performed in an analogous fashion to those reported previously.[1] For each molecule we first performed a standard SCF calculation near the experimental equilibrium geometry.[3,4] The structural formulae of the molecules are collected in Figure 1. The basis sets (S/C, N, O/H) of (12*s* 8*p*/10*s* 5*p*/4*s*) primitive Gaussians contracted to [6*s* 4*p*/3*s* 2*p*/2*s*] were taken directly from Dunning and Hay.[5]

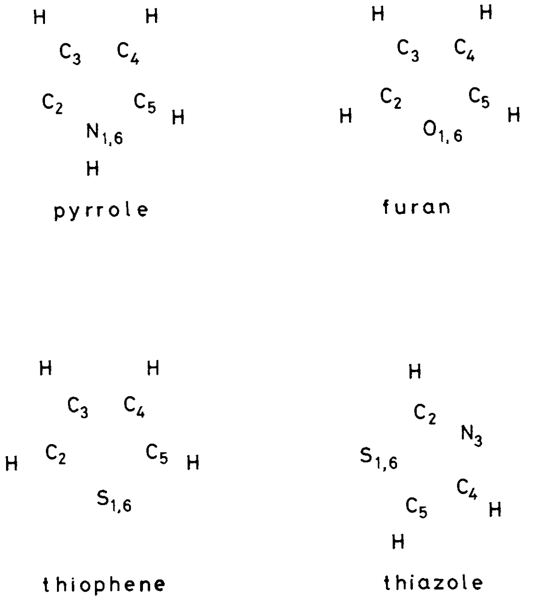


Figure 1. Structural formulae of the heterocyclic molecules pyrrole, furan, thiophene, and thiazole. The molecules have been drawn to scale

In the spin-coupled calculations on pyrrole and furan, the 30 σ electrons were accommodated in doubly occupied SCF orbitals and the six π electrons were described by six non-orthogonal singly occupied orbitals expanded in the basis comprising all the π MOs. The orbitals were fully optimized with no orthogonality constraints of any type, and all five spin couplings were included for six electrons with zero total spin. At convergence, the spin-coupled orbitals were transformed back to the atomic orbital basis for interpretation and plotting. For thiophene and thiazole, the two π electrons corresponding to 2*p* functions on sulphur were also included in the 'core'; the six valence π electrons are automatically orthogonal to this core because of the use of the MO basis.

Electronic Structure

The spin-coupled description of the π electrons in pyrrole corresponds to an energy lowering relative to the SCF solution of 165 kJ mol^{-1} (see Table 1). The spin-coupled orbitals are shown in Figure 2; there is one orbital localized on each carbon

Table 1. Spin-coupled and SCF total energies for heterocyclic molecules with five-membered rings. The energy lowerings and 'resonance energies,' as defined in the text, are also recorded

	Total energy (hartree)		Lowering	Resonance energy
	SCF	Spin-coupled	(kJ mol^{-1})	(kJ mol^{-1})
Pyrrole	−208.296 550	−208.359 571	165	31
Furan	−228.087 031	−228.156 707	183	11
Thiophene	−546.436 993	−546.496 584	156	25
Thiazole	−562.494 346	−562.559 252	170	34

Table 2. Occupation numbers (%) in the Rumer basis for heterocyclic molecules with five-membered rings

	R_4	R_5
Pyrrole	80	20
Furan	85	15
Thiophene	88	12
Thiazole	85	11

Table 3. Comparison of the simplest SCF and VB estimates of ionization potentials with experimental data[3]

	Ionization potential (eV)		
	Simplest VB	Koopmans' theorem	Experiment
Pyrrole	9.3	9.4	8.2
	9.7	10.3	9.2
	14.0	16.4	
Furan	10.5	10.3	8.9
	11.5	12.1	10.3
	15.5	18.3	14.4
Thiophene	9.8	10.3	8.9
	10.1	10.4	9.5
	13.6	15.5	12.1

atom and one on the heteroatom. The sixth orbital is also associated with the heteroatom but is very significantly distorted and shows delocalization onto the neighbouring carbon atoms. The overlap integrals between the different spin-coupled orbitals are reported in Table 4.

For all the molecules considered in the present work, the only important spin functions in the Rumer basis are R_4 and R_5 which correspond to singlet coupling of the two electrons on the heteroatom. In a description based on orbitals fully localized on each atom, we can identify the Rumer functions R_4 and R_5 with the classical valence bond structures (**1**) and (**2**), respectively.

(**1**)

(**2**)

When the orbitals cease to be completely localized, as turns out to be the case for one of the orbitals on the heteroatom, this interpretation ceases to be precise. However, with this reservation, structures (**1**) and (**2**) for pyrrole contribute *ca.* 80 and 20%, respectively. The distortion of the orbitals on carbon is consistent with the dominance of VB structure (**1**). Using the same orbitals, the energy of the dominant spin coupling is −208.347 751 hartree, which is 31 kJ mol^{-1} higher than the full solution. This stabilization energy might reasonably be termed the resonance energy and it is this, rather than delocalized orbitals, that distinguishes aromatic systems from other molecules. This definition, which is based on the geometry of (and the orbitals in) the full solution, emphasizes most clearly the importance of the mode of spin coupling. A less appropriate, alternative energy difference based on reoptimization of the orbitals in the case with one spin function would produce smaller values for this resonance energy.

Table 4. Overlap integrals between spin-coupled orbitals for pyrrole, furan, thiophene, and thiazole. The numbering of the orbitals coincides with that in Figure 1. Orbitals φ_1 and φ_6 both stem from the same heteroatom; they are the compact orbital and the more distorted orbital, respectively

Pyrrole	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	−0.36	−0.30	0.30	0.36	0.81
φ_2		1	0.72	−0.42	−0.30	−0.50
φ_3			1	−0.47	−0.42	−0.23
φ_4				1	0.72	0.23
φ_5					1	0.50
φ_6						1

Furan	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	0.28	0.20	0.20	−0.28	−0.82
φ_2		1	0.67	−0.25	−0.17	−0.43
φ_3			1	−0.38	−0.25	−0.12
φ_4				1	0.67	0.12
φ_5					1	0.43
φ_6						1

Thiophene	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	0.42	0.48	−0.48	−0.42	−0.88
φ_2		1	0.72	−0.28	−0.23	−0.57
φ_3			1	0.42	−0.28	−0.38
φ_4				1	−0.72	−0.38
φ_5					1	0.57
φ_6						1

Thiazole	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	0.46	−0.50	−0.49	−0.42	0.87
φ_2		1	0.71	−0.30	−0.24	0.65
φ_3			1	−0.42	0.28	−0.44
φ_4				1	0.72	−0.39
φ_5					1	−0.55
φ_6						1

The spin-coupled description of furan is similar to that of pyrrole. The major difference is that the second orbital on the heteroatom is very much more localized in this case (see Figure 3 and Table 4). The occupation numbers in the Rumer basis are listed in Table 2 and show a slightly larger contribution from structure (**1**) than is the case for pyrrole. Although the energy difference between the spin-coupled and SCF descriptions is larger than for pyrrole (183 kJ mol^{-1}) we find that the resonance energy in this case is only 11 kJ mol^{-1}.

Thiophene is also similar to pyrrole and in this case the second electron on the heteroatom shows even more delocalization onto the neighbouring centres (see Figure 4). The energy lowering in this case (Table 1) is again quite similar and the occupation numbers in the Rumer basis are listed in Table 2. Although spin coupling R_4 is even more dominant than is the case for furan, the resonance energy of 25 kJ mol^{-1} is somewhat

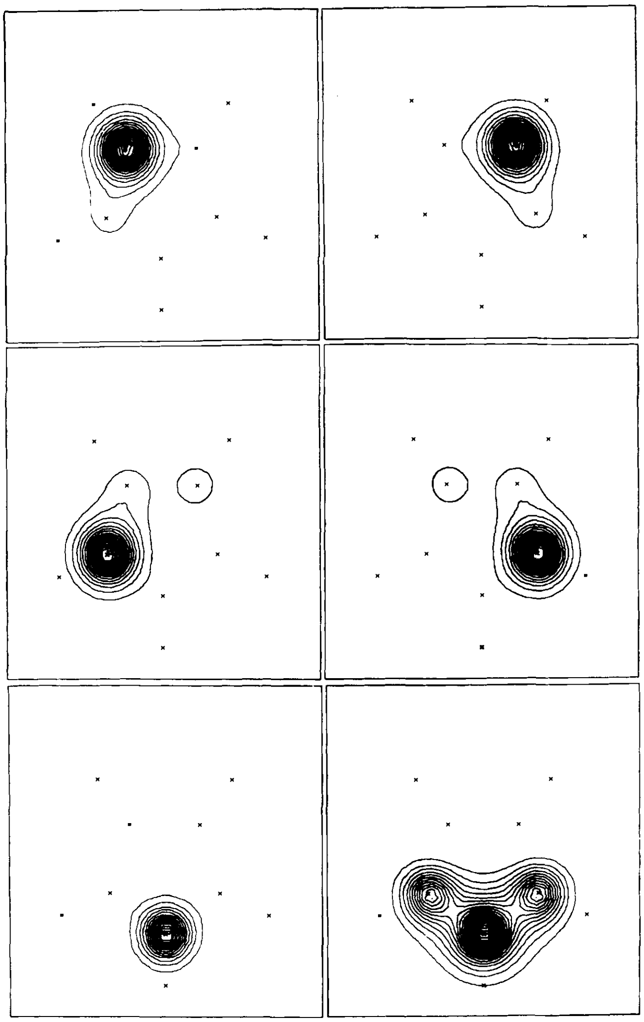


Figure 2. Spin-coupled orbitals in pyrrole in the plane one unit of atomic distance (*ca.* 0.529 Å) above the molecular plane. Throughout this work we plot the square modulus of the orbitals, $|\varphi_\mu(r)|^2$

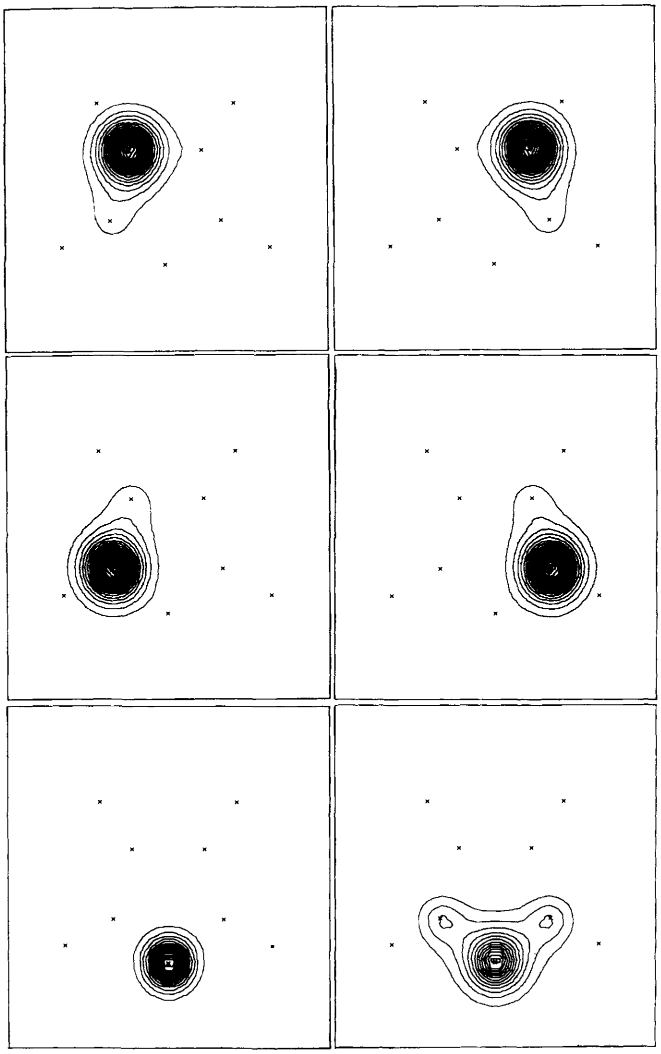
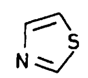


Figure 3. Spin-coupled orbitals in furan. The view has the same orientation as in Figure 1 and is analogous to that in Figure 2

larger. There does not seem to be a simple connection between the occupation numbers and our definition of resonance energy. In addition, the energy differences between the spin-coupled and SCF descriptions does not appear to correlate with the resonance energy.

It is highly unlikely that extension of the basis sets employed here will lead to significant changes in any of our conclusions. However, the inclusion of polarization functions will almost certainly lead to small changes in the values that have been quoted for energy differences, resonance energies, and occupation numbers.

Thiazole differs from thiophene by the replacement of one of the C–H units by a pyridine-like nitrogen atom. The calculated energies for this molecule are listed in Table 1. In this case, the spin-coupled description corresponds to an energy *ca.* 170 kJ mol^{-1} lower than that afforded by MO theory. The spin-coupled orbitals are shown in Figure 5 and it is clear that there are marked similarities to thiophene. Five of the orbitals are very localized, with one on each main atom. The distortion of these orbitals and the overlaps between them (Table 4) are consistent with the dominance of the structure (**3**). This is borne out by the occupation numbers in the Rumer basis (Table 2) although the direct interpretation of these in terms of the VB structures (**1**) and (**2**) is not precise. This is because the sixth orbital, which is centred on the sulphur atom, shows very large distortion and is significantly delocalized onto the neighbouring carbon atoms. Note that in this case there are small contributions (a total of 4%) from spin functions R_2 and R_3.



(**3**)

For all the molecules considered here, we performed also a small 'non-orthogonal configuration interaction' (CI) or 'spin-coupled VB' calculation. This included the spin-coupled configuration and all singly ionic configurations. This resulted in very small additional energy lowerings of <2 millihartree. As explained in the previous paper, even these values overestimate the significance of ionic structures. If the orbitals are free to distort, or even to delocalize over more than one centre, spin-coupled ionic structures are not important in these aromatic molecules.

Photoelectron Spectroscopy

Great use is made of the fact that SCF molecular orbitals belong to a given irreducible representation of the molecular point

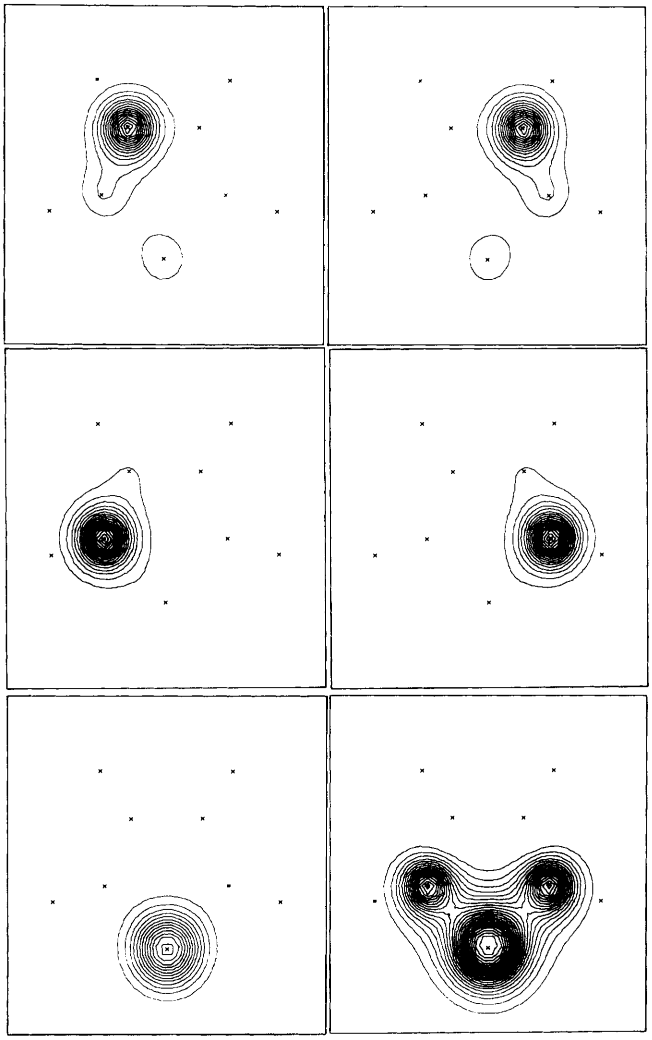


Figure 4. Spin-coupled orbitals in thiophene. The view has the same orientation as in Figure 1 and is analogous to that in Figure 2

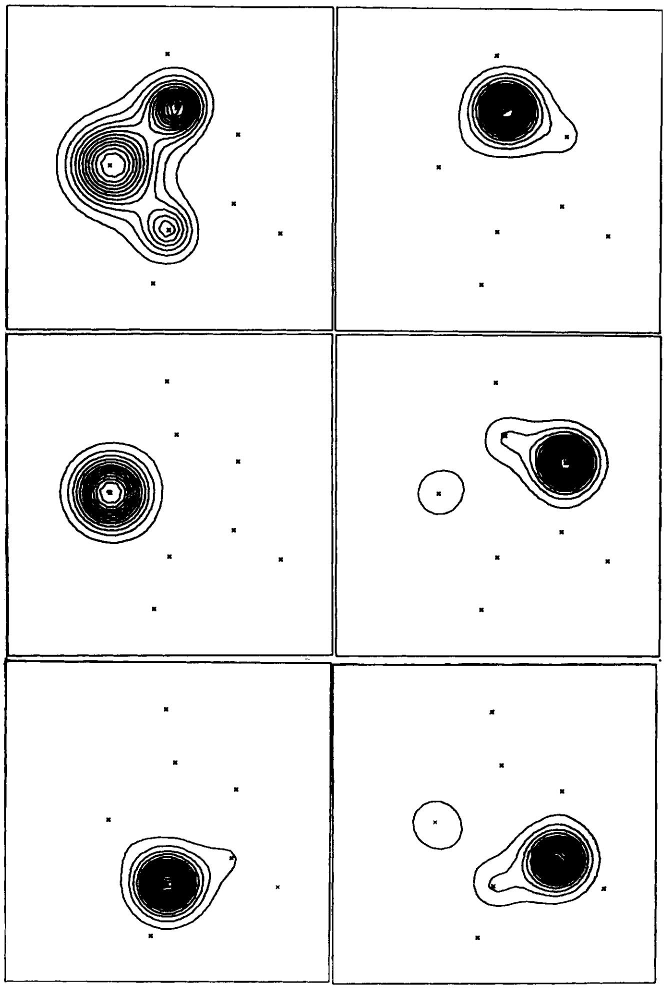


Figure 5. Spin-coupled orbitals in thiazole. The view has the same orientation as in Figure 1 and is analogous to that in Figure 2

group, even though the wavefunction is invariant to linear transformations which remove symmetry properties. For example, the canonical MOs are very convenient for the interpretation of photoelectron spectroscopy (PES) experiments. However, there is nothing inconsistent between the spin-coupled description of a molecule and its PES spectrum. Removal of an electron from a localized orbital may produce a wavefunction for the ion which lacks the necessary spatial symmetry. One simply takes an appropriate linear combination of the different 'hole states'.[6] Of course, the detailed interpretation of the PES data in any approach requires separate calculations on the neutral molecule and on the different states of the ion.

It is interesting to compare the simplest MO and the simplest VB estimates of ionization potentials. In the case of molecular orbital theory, Koopmans' theorem approximates the ionization potential with an SCF orbital energy. This corresponds to removing one electron from a particular molecular orbital without allowing the others to relax, and it ignores differences in correlation energy between the two species. Nonetheless, estimates based on Koopmans' theorem have proved useful guides to the initial assignment of PES peaks. The approximations inherent in Koopmans' theorem are sometimes overlooked, and many papers still appear in the literature in which different states of an ion are strictly interpreted in terms of differences in orbital energies.

The simplest calculation, and the nearest equivalent in our approach, is to construct a wavefunction for the ion using the spin-coupled orbitals for the neutral molecule but taking away one electron in all possible ways. For these systems with six π electrons, there are six such 'hole states', although not all will be important for describing the ion. A very inexpensive non-orthogonal CI calculation on these hole states produces energies for low-lying states of the ion.

We have applied this simple approach to pyrrole, furan and thiophene. The ionization potentials shown in Table 3 are very convincing. The simple valence bond estimates are slightly better than those from Koopmans' theorem for the lowest state of the ion. Using these orbitals optimized for the neutral molecule, all the hole states contribute for furan and pyrrole except for that arising from removal of the more localized orbital on the heteroatom. For thiophene, the important hole states correspond to the removal of an electron from sulphur. In this simple VB approach, the error is roughly the same in each state, but Koopmans' theorem becomes steadily worse for the higher states of the ion.

More accurate values would require a larger basis set and separate calculations on each state which take some account of electron correlation in the ion. We shall report in due course the spin-coupled orbital picture for ions of aromatic molecules.

Conclusions

We have shown that the spin-coupled descriptions of furan, pyrrole, thiophene, and thiazole are very similar to those for benzene and for six-membered heterocycles. The π electrons in all of these systems are described well in terms of localized but non-orthogonal orbitals, and the characteristic stability results from the mode of spin coupling. A special feature of the present series of molecules is the distinct tendency for one of the orbitals stemming from the heteroatom to show very significant distortion to an extent that depends on the electronegativity. We now have a consistent and highly visual model of the behaviour of correlated electrons for a whole range of heteroaromatic molecules. This approach will be extended to the inorganic rings borazine $B_3N_3H_6$ and boroxine $B_3O_3H_3$ in a forthcoming publication, where the relationship between spin-coupled and MO CI wavefunctions will also be examined.[7]

A particularly successful aspect of this paper is the straightforward estimate of ionization potentials by spin-coupled theory. This is based upon physical assumptions which closely parallel those of MO theory. The results for the lowest ionization potentials are at least as good as those derived from Koopmans' theorem, while the higher potentials appear to be a good deal more reliable.

We shall return to this development of the theory in later work. Our future publications will also deal in detail with excited states of the neutral molecules, but will concentrate on other aspects of aromaticity such as the $4n + 2$ rules, the anisotropy in the diamagnetic susceptibilities ('ring currents'), and substituent effects.

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