

The Electronic Structure of Heteroaromatic Molecules. Part 1. Six-membered Rings

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Spin-coupled theory is applied to the π electrons of benzene and of the heteroaromatic molecules pyridine, pyridazine, pyrimidine, and pyrazine. A companion paper deals with five-membered rings. The spin-coupled wavefunction is very flexible and includes the familiar delocalized molecular orbital description as just one of the many special cases to which our calculations might converge. The actual solutions correspond to energies considerably lower than those afforded by molecular orbital (MO) theory and consist of localized orbitals which are clearly deformed C(2p) or N(2p) functions. This provides a clear picture of the behaviour of correlated electrons in systems of this kind. The special stability of aromatic molecules arises from the mode of spin coupling and not from delocalized orbitals. Except for small but crucial distortions of the orbitals, there is a marked similarity to the classical valence bond (VB) descriptions of these systems. The spin-coupled representation of benzenoid heterocyclic systems incorporates a great deal of electron correlation while still retaining a clear-cut visuality. At the very least, it must now be regarded as a credible alternative to the MO-based view of these molecules and there are good reasons to reconsider our attitudes to the classical VB descriptions of these systems.

For more than a quarter of a century, most organic chemists have held a somewhat ambivalent view of the relative merits of molecular orbital (MO) and valence bond (VB) theory. Nowhere is this more apparent than in the electronic structure of aromatic molecules. Our understanding of such systems has been dominated by the MO self-consistent field (SCF) model in which electrons move more or less independently of one another in delocalized orbitals. In simplified form, this model leads to the $4n + 2$ rule of Hückel theory. The SCF picture provides a simple rationalization of the special stability of aromatic molecules, and of their n.m.r. and photoelectron spectra.

A serious drawback of simple MO theory is its inability to treat correctly the making and breaking of chemical bonds. When correlation between electrons cannot be ignored, particularly in cases such as these, a multiconfiguration wavefunction with much configuration interaction (CI) becomes necessary. Any vestige of a physical picture soon vanishes, and with it all our fundamental chemical insight into problems.

Not surprisingly, it has become the tradition to represent reaction mechanisms in terms of classical VB structures with localized bonds. At the simplest level, valence bond ideas lead to correct predictions of the products from aromatic substitution reactions, without recourse to any calculations. An attitude fostered by many undergraduate texts is that the valence bond description is much easier to understand and to use, but that molecular orbital theory is in some sense more fundamental. Some organic chemists will admit to a slight feeling of unease when using VB arguments in discussions with theoreticians.

The purpose of this work is to present clear theoretical evidence which challenges much of the accepted wisdom. In a preliminary account,¹ we have shown that the six π electrons in the benzene molecule are much better described in terms of localized non-orthogonal orbitals than by MO theory. The characteristic properties of this molecule arise not from delocalized orbitals but from a much more profoundly quantum

phenomenon, namely the mode of coupling of the electron spins. This picture is furnished by spin-coupled theory which incorporates a great deal of electron correlation while retaining a clear-cut visuality. In this paper we show that our previous results for benzene, which show a marked similarity to the familiar classical VB description, are by no means unique. We



consider the six-membered heterocycles pyridine, pyridazine, pyrimidine, and pyrazine. A companion paper is devoted to the five-membered rings furan, pyrrole, thiophene, and thiazole.² Our object is to build up a coherent picture of the structure and properties of a series of aromatic molecules on the basis of spin-coupled theory.

We provide a brief overview of the formalism of our approach in the next section, concentrating on a qualitative description of the most characteristic features of the theory. Further details may be found in the literature cited and in a recent extensive review.³

The general picture of heterocyclic molecules which emerges from the present work is very different from that of the conventional MO-based model. The spin-coupled representation of benzenoid heterocyclic systems incorporates a considerable degree of electron correlation and it is, to all intents and purposes, unaltered by the inclusion of additional electron correlation *via* configuration interaction. At the very least, our model must be considered as a credible alternative to the MO-based view of these molecules and there are good reasons to reconsider our attitudes to the classical VB descriptions of these systems.

Spin-coupled Theory.—In the spin-coupled description of a system with N electrons, the orbitals are all non-orthogonal with a single electron per orbital. The N orbitals are written as general linear combinations of atomic orbitals drawn from all the nuclei comprising the molecule, much as in MO theory. No preconceptions are imposed as to the final form of the spin-coupled orbitals, which may be as localized or delocalized as is necessary to give the lowest energy.

Since there is only one electron per orbital, it is essential to allow for all the possible ways of coupling together the individual electron spins to form the required resultant spin. This is a new feature which is necessarily absent in MO theory and involves the use of a linear combination of N -electron spin functions. Together with the non-orthogonality of the orbitals, this provides much of the power of the spin-coupled description and is of critical importance in providing the correct topology of potential surfaces. As the nuclei move, the presence of different spin functions allows the electron spins to uncouple from one another as old bonds disintegrate, and then to recouple with each other as new bonds form. This is, of course, the central phenomenon in a Diels–Adler reaction, for example. The same feature of spin recoupling enables the spin-coupled wavefunction to provide a correct and very compact description of all the possible modes of dissociation of a molecule.

In spin-coupled theory, a system of N electrons is described by N distinct non-orthogonal orbitals whose spins are coupled to the required overall resultant S (and projection M) according to a particular coupling scheme k . The final spin-coupled wavefunction Ψ_{SM} is a linear combination of all the possible coupling schemes k so that⁴ equation (1) holds

$$\begin{aligned}\Psi_{SM} &= \sum_k c_{Sk} \mathcal{A}[\varphi_1(r_1)\varphi_2(r_2) \dots \varphi_N(r_N)\Theta_{SM;k}^N] \\ &\equiv \{\varphi_1\varphi_2 \dots \varphi_N\}\end{aligned}\quad (1)$$

where c_{Sk} are called spin-coupling coefficients, \mathcal{A} is the antisymmetrizer, and $\Theta_{SM;k}^N$ is a coupled N -electron spin function. The spin functions (and thus the total wavefunction) are eigenfunctions of the operators for the square of the total spin \hat{S}^2 , and of the projection of the spin onto an arbitrary space-fixed z -axis, \hat{S}_z . All the variational parameters, namely the coefficients of the basis functions comprising the orbitals and the coefficients of the different N -electron spin functions, are optimized simultaneously so as to minimize the energy.

The form of the spin-coupled wavefunction is very flexible and actually includes the SCF wavefunction as a special case. The improvement of the energy over that given by a Hartree–Fock SCF calculation is usually very large and arises from the effects of electron correlation. The orbitals in MO theory are optimized subject to the constraint that they must all be orthogonal to one another. There are no physical reasons for this constraint, which was introduced as a computational convenience. In general, the ground state of a molecule corresponds to double occupancy of the individual SCF molecular orbitals so that only the perfect-pairing spin function is considered. In addition to providing a correct description as bonds are made or broken, removal of the constraints of MO theory leads to an entirely different interpretation of molecular electronic structure.

This description may be refined by means of ‘non-orthogonal configuration interaction’ which allows excitations from one or more occupied orbitals into excited-state or virtual solutions. We refer to these further calculations, which produce total energies and molecular properties of comparable accuracy to those from the most sophisticated MO-CI techniques, as spin-coupled VB wavefunctions. In all the many cases studied so far, the spin-coupled wavefunction based on just one spatial configuration provides all the correct features of the potential surfaces and remains overwhelmingly dominant in the final spin-

coupled VB wavefunction for all geometries. Consequently, the spin-coupled description carries real conviction, in the sense that the inclusion of further correlation effects does not alter the essential physical picture.

The Electronic-Structure of Benzene.—A brief, preliminary account of our work on benzene has been presented elsewhere.¹ The spin-coupled calculations on the heteroaromatic molecules were performed in an analogous fashion to those for benzene. We start with a summary of our previous calculations, in order to facilitate the later discussion.

For all the molecules considered in this work, we include the effects of electron correlation for the π electrons but not for the σ framework. The electrons of the σ framework are described by a set of doubly occupied SCF molecular orbitals, and spin-coupled theory is used explicitly only for the six π electrons. This σ – π separation is an approximation whose utility rests upon the chemistry of aromatic systems—to abandon it would be to ignore this entire body of experience. Furthermore, extensive CI calculations⁵ have demonstrated that ‘valence only’ correlation affords an excellent description of ground and excited states of benzene. It is found that further small improvements require σ – π correlation, rather than σ correlation itself. We shall return later to the question of the σ – π separation in our calculations.

Spin-coupled calculations were performed on benzene near its equilibrium geometry using a basis set of (10s 5p/4s) Gaussian functions contracted to [3s 2p/2s]. The basis set was taken directly from the tables of Dunning and Hay,⁶ without any scaling of the hydrogen exponents. As mentioned above, the 36 electrons of the σ framework were accommodated in doubly occupied molecular orbitals taken from a standard SCF procedure. The π electrons were described by six distinct non-orthogonal orbitals which were expressed as completely general linear combinations of all the basis functions of π symmetry. This is equivalent to expanding the π orbitals in a basis set consisting of the 12 SCF delocalized π orbitals, occupied and unoccupied. The total wavefunction takes the form (2). For a

$$\Psi = \sum_k c_{0k} \mathcal{A}(\sigma_1^2 \sigma_2^2 \dots \sigma_{18}^2 \pi_1 \pi_2 \pi_3 \pi_4 \pi_5 \pi_6 \Theta_{0,0;f}^{36} \Theta_{0,0;k}^6) \quad (2)$$

system of six electrons with a net spin of zero there is a total of five possible spin couplings, all of which were included. Our calculations were performed using the Kotani or branching-diagram scheme and correspond to an expansion in the *complete* spin space. For a discussion of different spin functions, and of the relationships between them, see for example the book by Pauncz.⁷

The form of wavefunction (2) encompasses a very wide range of possible solutions with varying degrees of delocalization. The SCF solution is just one such possibility. We find that the converged spin-coupled wavefunction for benzene consists of six highly localized orbitals which all possess an identical energy and shape. They can be transformed into one another by successive \hat{C}_6 rotations. The spin-coupled orbitals in benzene are essentially deformed $C(2p_z)$ orbitals which are distorted symmetrically towards the neighbouring carbon atoms on each side (see Figure 1). The spins are coupled symmetrically around the ring to give the correct overall X^1A_{1g} state—all five spin functions contribute. The energy lowering relative to the MO solution is 0.0750 hartree (197 kJ mol^{−1}), which is considerable. We found that the energy lowerings and that the form of the orbitals from a calculation using a slightly larger [3s 3p/2s] basis were very similar.

The relative importance of the different spin functions for benzene was examined by transforming our results to the more traditional basis of Rumer functions used in classical VB theory. These functions are specified in a little more detail later. For

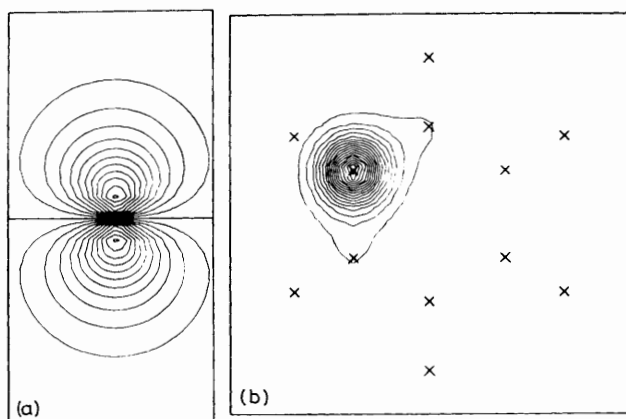


Figure 1. Spin-coupled orbitals in benzene: (a) in a σ_v mirror plane, (b) in the plane one unit of atomic distance (*ca.* 0.529 Å) above the σ_h molecular plane. Throughout this work we plot the square modulus of the orbitals, $|\varphi_\mu(r)|^2$

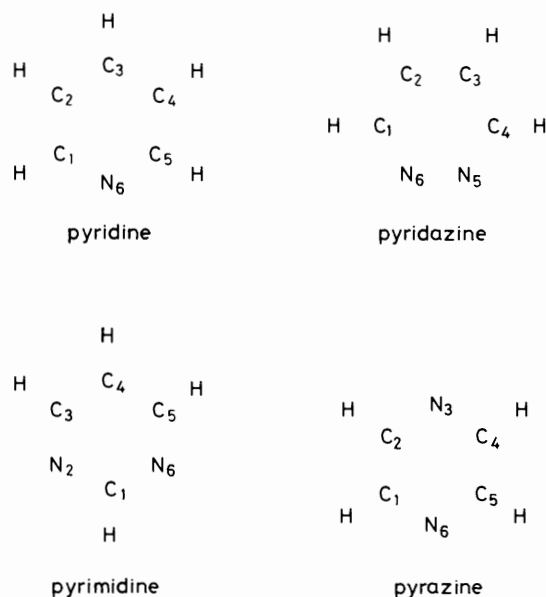


Figure 2. Structural formulae of the heteroaromatic molecules pyridine, pyridazine, pyrimidine, and pyrazine. The molecules have been drawn to scale

benzene, spin couplings corresponding to Kekulé structures contribute 40.5% each and those corresponding to *para*-bonded or Dewar structures contribute 6.5% each.

The Kekulé description of benzene, as expressed in the classical VB form, appears to be much closer to reality than is a description in terms of delocalized molecular orbitals, and it provides a clear picture of the behaviour of *correlated* electrons in this molecule. The special properties of benzene arise fundamentally from the symmetric coupling of the electron spins around the carbon ring framework. Except for small but crucial distortion of the orbitals, the spin-coupled and classical VB descriptions of this molecule are very similar.

In the MO description of benzene, the (canonical) orbitals are all determined as eigenfunctions of a simple operator \hat{F} (the Hartree-Fock operator). Consequently, they are orthogonal and the lowest energy state of the molecule is obtained when the individual molecular orbitals are doubly occupied. As a direct result of these restrictions, the orbitals have symmetries

corresponding to irreducible representations of the D_{6h} point group. In an SCF calculation with only a single $2p_z$ basis function on each carbon atom, the delocalized orbitals are completely determined by symmetry alone.

The SCF wavefunction is invariant to linear transformations of the orbitals but, at least in the case of benzene, it proves impossible to localize them completely. When the restrictions of MO theory are lifted, the orbitals of benzene become highly localized. It is important to note that the spin-coupled wavefunction is not invariant to linear transformations of the orbitals, so that their form is unique and is determined solely by optimizing the variational parameters.

Calculations

In order to establish a numbering scheme and to define the orientations of the molecules, the structural formulae of the molecules considered in this work are collected in Figure 2. For each molecule we first performed a standard SCF calculation near the experimental equilibrium geometry using contracted Gaussian basis sets taken directly from the work of Dunning and Hay. Bond lengths and angles were taken from the volumes edited by Katritzky and Rees,⁸ but where we were unable to find precise C-H bond lengths we took values from related molecules. The σ electrons were accommodated in doubly occupied SCF molecular orbitals and the π electrons were described by six non-orthogonal singly occupied orbitals expanded in the basis comprising all the π MOs.

Most of the computer resources (both processor time and disk space) were involved in the calculation of atomic integrals over the Gaussian basis set. It is this feature that has precluded the use of larger basis sets in the present work. By comparison, the spin-coupled calculations used trivial amounts of computer time (a few seconds on a scalar computer) and were run online. It is most unlikely that extension of the basis sets would affect any of the conclusions reached here.

Results

As our first new example of the application of spin-coupled theory to aromatic systems we consider the pyridine molecule which has C_{2v} symmetry and whose π molecular orbitals are delocalized much as in benzene. The SCF and spin-coupled energies are shown in Table 1; the energy lowering of 0.081 hartree (*ca.* 210 kJ mol⁻¹) is even larger than that for benzene. It is clear that the large value for benzene is not merely a reflection of the high point-group symmetry. The spin-coupled orbitals for pyridine (Figure 3) are localized and take the form of slightly distorted $2p$ functions pointing perpendicular to the molecular plane. The carbon orbitals are very similar to those in benzene but the nitrogen orbital shows less distortion towards its neighbours. The overlaps between the spin-coupled orbitals are reported in Table 3.

All five spin couplings contribute in the spin-coupled description of pyridine. It is probably easiest to visualize the relative importance of these in terms of the Rumer functions shown in Figure 4. An arrow between points i and j on the circle signifies that electrons i and j are singlet coupled, and $i \rightarrow j$ corresponds to the occurrence of a factor (3) in the spin function.

$$(1/\sqrt{2})[\alpha(i)\beta(j) - \beta(i)\alpha(j)] \quad (3)$$

The occupation numbers in the Rumer basis are reported in Table 2, where the ordering of the orbitals coincides with the numbering of the atoms in Figure 2. The spin couplings that correspond to Kekulé structures contribute 40% each, the two equivalent Dewar structures 7.5% each, and the remaining

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

	Total energy (hartree)		Lowering (kJ mol ⁻¹)	Resonance energy (kJ mol ⁻¹)
	SCF	Spin-coupled		
Benzene	-229.995 39	-230.070 43	197	92
Pyridine	-246.049 07	-246.129 84	212	92
Pyridazine	-262.081 75	-262.170 13	232	56
Pyrimidine	-262.096 79	-262.183 19	227	95
Pyrazine	-262.085 85	-262.173 14	229	94

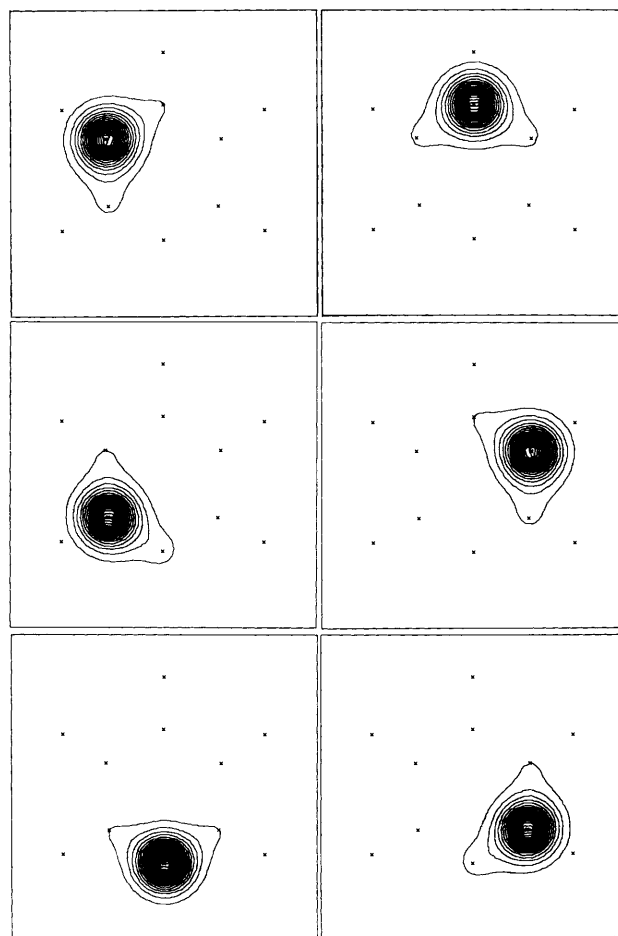
Table 2. Occupation numbers of the different spin couplings in the Rumer basis for heterocyclic molecules with six-membered rings. The Rumer diagrams (R_i) are numbered as in Figure 4

	Occupation numbers (%)				
	R_1	R_2	R_3	R_4	R_5
Benzene	40.5	6.5	6.5	40.5	6.5
Pyridine	40	7.5	5.5	40	7.5
Pyridazine	20.5	8.5	8.5	54	8.5
Pyrimidine	40	8.5	6	40	6
Pyrazine	40	8	4.5	40	8

Table 3. Overlap integrals between spin-coupled orbitals for pyridine, pyridazine, pyrimidine, and pyrazine. The numbering of the orbitals coincides with that in Figure 2

Pyridine						
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	0.51	-0.06	-0.15	0.11	-0.53
φ_2		1	-0.51	-0.02	-0.15	0.06
φ_3			1	-0.51	-0.06	-0.08
φ_4				1	0.51	-0.06
φ_5					1	0.53
φ_6						1
Pyridazine						
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	0.40	-0.03	0.10	-0.12	-0.59
φ_2		1	-0.61	-0.03	0.07	0.06
φ_3			1	0.41	0.06	-0.07
φ_4				1	0.59	0.10
φ_5					1	0.41
φ_6						1
Pyrimidine						
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	-0.51	0.09	-0.17	0.09	0.51
φ_2		1	-0.52	-0.02	-0.09	-0.08
φ_3			1	0.51	-0.07	-0.09
φ_4				1	-0.51	0.02
φ_5					1	-0.52
φ_6						1
Pyrazine						
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_1	1	-0.50	-0.06	0.16	0.04	0.52
φ_2		1	0.52	-0.04	0.16	-0.06
φ_3			1	-0.52	-0.06	0.48
φ_4				1	0.50	0.06
φ_5					1	0.52
φ_6						1

Dewar structure 5.5%. The valence bond structure based on the spin-coupled orbitals but using only the first Rumer function (Kekulé-type) has an energy of -246.094 645 hartree. It follows that the stabilization of the full solution over one based on the single most important spin coupling (but using the same orbitals) is 92.4 kJ mol⁻¹. It is not unreasonable to refer to this value as the resonance energy, if such a quantity is required,

**Figure 3.** Contour plot of spin-coupled orbitals in pyridine. The view is analogous to that in Figure 1(b) and has the same orientation as in Figure 2

and the characteristic stability of an aromatic system such as pyridine is linked directly to the magnitude of this energy difference. This definition emphasizes the importance of the mode of spin coupling and is more appropriate than an alternative energy difference based on reoptimization of the orbitals with just one spin function.

One of the most unacceptable features of classical VB theory is the apparent importance of ionic structures even in obviously covalent situations. This results from the fact that the orbitals in classical VB calculations have fixed atomic or hybridized form and are not allowed to distort. Ionic structures in spin-coupled theory are those which involve double occupancy of one or more orbitals. In our spin-coupled study of benzene we found that the inclusion of all possible ionic structures (a full CI in the

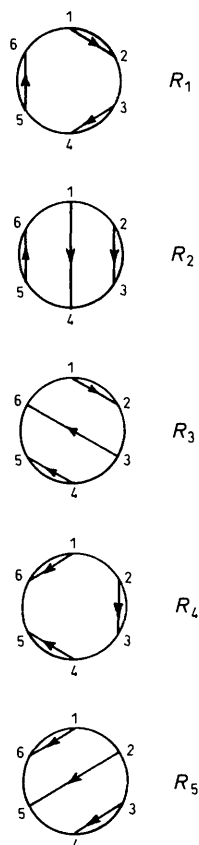


Figure 4. Rumer diagrams for $N = 6$, $S = 0$

π valence space) produced only a very small additional energy lowering. The orbitals in spin-coupled theory are allowed to distort as much or as little as is required to minimize the energy. The distortion of the orbitals corresponds to a small degree of delocalization over more than one centre. If the wavefunction is projected onto a basis of VB structures in which each orbital uses basis functions centred on just one atom, then the contributions from ionic structures reappear.⁹ In general, we find that spin-coupled ionic structures are not important except for describing charge-transfer effects in excited states.

For pyridine we performed a small non-orthogonal CI (spin-coupled VB) calculation which included the spin-coupled structure and all singly ionic configurations. This produced a small additional energy lowering of < 3 millihartree. In actual fact, even this value represents an overestimate of the significance of ionic structures. If additional electron correlation is included by allowing excitations into virtual orbitals, the contributions from ionic structures are reduced still further. One of the main conceptual objections to this type of description of aromatic systems is thus removed.

The replacement of one C-H unit in benzene by a nitrogen atom results in small changes in the form of the spin-coupled orbitals and in the relative importance of the different spin couplings of the π electrons. It seems very worthwhile to investigate whether the diazabenzenes have similar descriptions. The total energies from SCF and spin-coupled calculations on these molecules are recorded in Table 1. The energy lowerings for pyridazine, pyrimidine, and pyrazine are 232, 227, and 229 kJ mol^{-1} , respectively. The inclusion of singly ionic structures resulted in insignificant further energy lowerings, as in the previous cases.

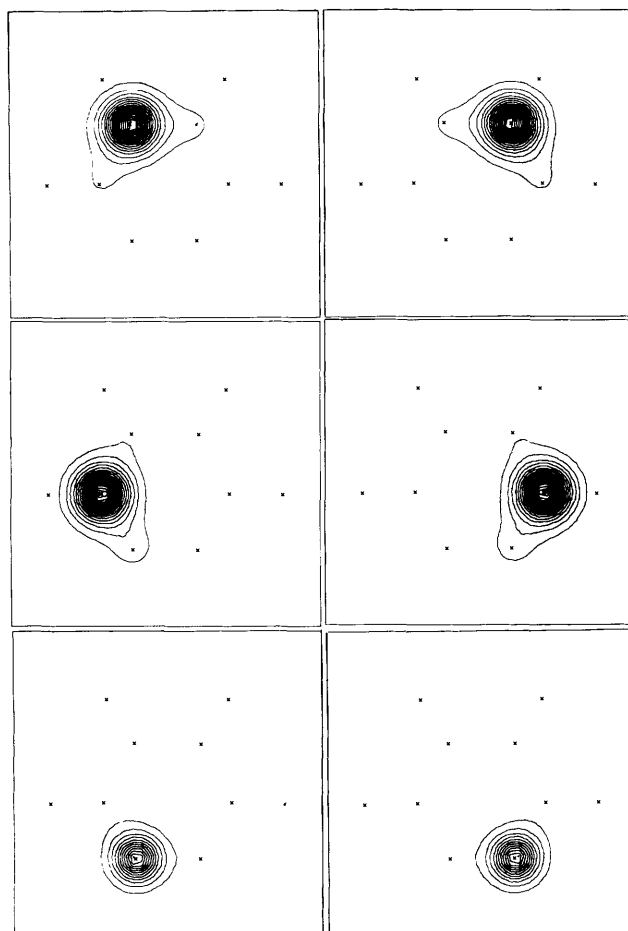


Figure 5. Spin-coupled orbitals in pyridazine. The view is analogous to that in Figure 1(b) and has the same orientation as in Figure 2

The spin-coupled orbitals for the diazabenzenes are shown in Figures 5–7. These are clearly distorted atomic $2p$ functions, pointing perpendicular to the molecular plane. The orbitals localized on symmetry-related centres are themselves transformed into one another by symmetry operations of the point group, and the relative distortion of carbon and nitrogen orbitals appears to reflect the difference in electronegativity of these atoms. The overlap integrals between the spin-coupled orbitals are listed in Table 3.

As before, the calculations were performed using the Kotani scheme but, for ease of interpretation, we report in Table 2 the occupation numbers in the Rumer basis. The orbitals are ordered according to the labelling of Figure 2. For pyridazine, the Kekulé structure with singlet coupling of π electrons on the adjacent nitrogen atoms contributes 20.5%, whereas the other Kekulé form has an occupation number of 54%. The three Dewar structures contribute *ca.* 8.5% each. For pyrimidine the two equivalent Kekulé structures contribute 40% each, the two equivalent Dewar structures 6% each, and the remaining Dewar structure 8.5%. The same pattern is shown for pyrazine: the Kekulé-type structures contribute 40% each, the two equivalent Dewar structures 8% each, and the remaining Dewar structure (with no C-N singlet couplings) only 4.5%.

Using the same definition of 'resonance energy' as for pyridine, we find stabilization energies for pyridazine, pyrimidine, and pyrazine of 56, 95, and 94 kJ mol^{-1} , respectively. These values correspond to the energy difference between the

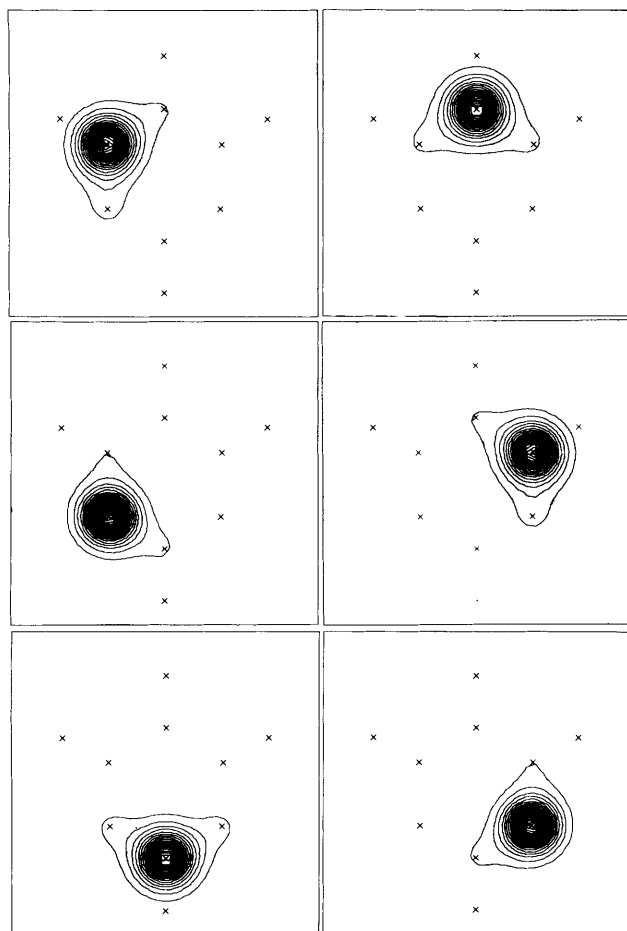


Figure 6. Spin-coupled orbitals in pyrimidine. The view is analogous to that in Figure 1(b) and has the same orientation as in Figure 2

dominant spin coupling and the full solution based on all five couplings, using the same orbitals in both cases. We conclude that the characteristic stability of aromatic molecules such as these is linked to the importance of the different spin couplings, and not to any supposed delocalization of the orbitals.

The occupation numbers of the different Rumer functions appear to be ordered according to simple rules. (a) The most important contributions are those from the Kekulé-type structures. (b) The next most important structures involve two C–N singlet couplings. It is often the case that the first two rules describe the same structures. (c) The third most important group of structures consists of those with one C–N singlet coupling. (d) All other structures make smaller contributions. The reasons behind this preference for singlet coupling between orbitals on carbon and nitrogen are not clear, although it is worth noting that the energy difference between single and double bonds is larger in the case of C–N than it is for C–C. Exceptions to these rules may well appear later, but they are consistent with all the heterocyclic systems studied near equilibrium geometry.

It is important to notice that although the Kekulé-type structures have the largest weights, there are significant contributions from all the modes of spin coupling. The situation may change very rapidly as soon as the bond lengths and bond angles vary. For example, calculations on a distorted pyrimidine molecule, with larger C1–N2 and C1–N6 distances, produce results which do not conform to the pattern described above. Although the spin-coupled orbitals are very similar to

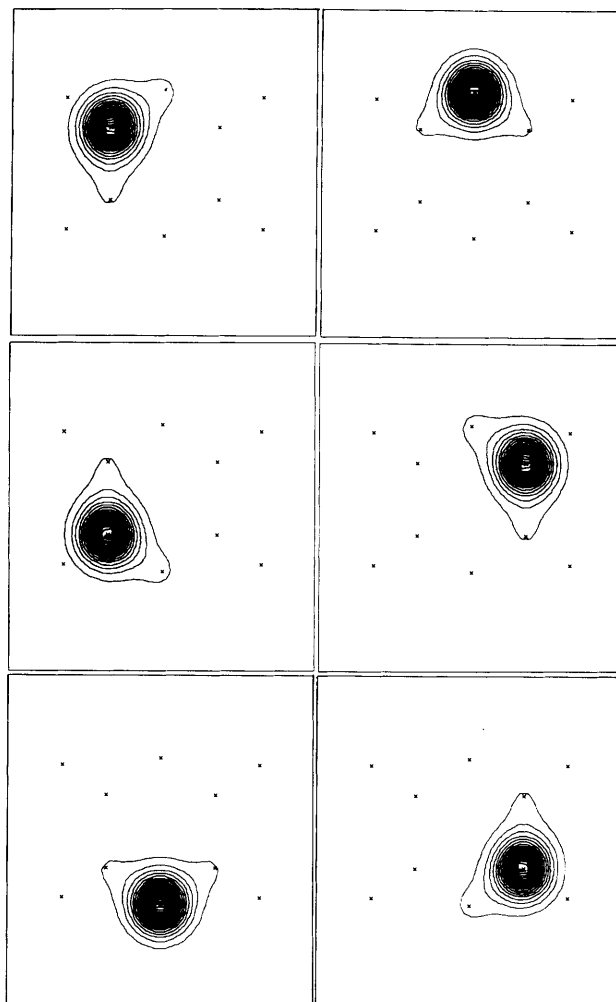


Figure 7. Spin-coupled orbitals in pyrazine. The view is analogous to that in Figure 1(b) and has the same orientation as in Figure 2

those at equilibrium geometry, the occupation numbers of the spin functions are totally different. In this case, the Kekulé-type structures contribute 21% each and the two equivalent Dewar structures contribute only 6% each. The single most important spin coupling for pyrimidine at this geometry actually corresponds to the remaining Dewar structure (46%), with two singlet couplings of C with N (orbital overlap of 0.63) and a weak C1–C4 bond (orbital overlap of 0.35) across the ring. Consequently, it is crucial to use the complete spin space in these calculations and *not* to allow one's preconceptions to decide which spin functions should be taken into account and which can be neglected.

The extension of the basis sets used in this work is unlikely to alter significantly any of our conclusions. However, the inclusion of polarization functions may lead to small changes in the values quoted for quantities such as resonance energies and occupation numbers.

Conclusions

In this paper we have applied spin-coupled theory to the π electrons of a series of six-membered heteroaromatic ring systems, pyridine, pyridazine, pyrimidine, and pyrazine. It is clear from this that the previous results for the benzene molecule¹ are by no means exceptional. In fact the energy lowerings over the SCF solutions for these azabenzene are even larger. The

contributions of the different spin couplings in these molecules generally conform to the pattern found for benzene with the added proviso of a marked preference for C=N bonds, and this seems entirely reasonable.

We return now to the question of the σ - π separation in our calculations. It has been suggested for benzene that the σ and π orbitals may mix to form 'banana'-shaped bonds.¹⁰ These conclusions arose from a calculation in which all the π electrons and some electrons from the σ framework were correlated. However, this calculation also involved a number of fairly drastic constraints or assumptions. Only six σ electrons were included, even though 12 σ electrons are expected to be involved in C-C bonding. Furthermore, all the electrons were placed in pairs such that orbitals in different pairs are orthogonal to one another. This is known as the strong orthogonality constraint. For 12 electrons with a net spin of zero, the total number of spin functions is very large (132) but only two of these were included, corresponding to Kekulé structures with singlet coupling of the electrons in the strongly orthogonal pairs. We have commented above on the importance of using the complete spin space. With all these constraints in mind, it is not clear whether the σ - π mixing is real or is merely an artifact of the calculation.

The calculations of Roos and his co-workers,⁵ as well as the chemistry of aromatic molecules, do not seem to be consistent with the idea of banana bonds. It has also been suggested, from similarly constrained calculations, that this form of σ - π mixing also occurs in molecules such as ethene and ethyne. Recent developments in the formulation of spin-coupled theory should allow us to perform full calculations on these systems without constraints and preconceptions. This will settle the question once and for all. We do not believe that significant σ - π mixing occurs in benzene.

Aromatic systems play a central role in organic chemistry, and a great deal of this has been fruitfully interpreted in terms of MO theory, that is, in terms of electrons moving more or less independently of one another in delocalized orbitals. The present work provides a clear model of the motion of *correlated* electrons in such systems. In order to avoid one another, the electrons occupy localized orbitals. But, and this is the central point, these orbitals are non-orthogonal (*i.e.* they overlap with one another), so that in spite of their local character, the electrons still influence one another. The special stability of these aromatic molecules arises from the mode of coupling of

the electron spins, as shown by the magnitudes of the resonance energies, and not from any supposed delocalization of the orbitals.

The fact that these kinds of orbitals are fully optimized gives them the form of slightly deformed C(2p) or N(2p) functions, pointing perpendicular to the molecular plane. The small distortions of the orbitals have the further consequence that the contribution of ionic structures disappears almost completely. One of the main objections to this type of description is thus removed. It is worth stressing that this last result is obtained by means of a 'non-orthogonal CI' calculation, and that the ability to make such refinements (and further ones if necessary) gives real conviction to this model.

Further conclusions and the outlook for future work are discussed in the companion paper. At the very least, the spin-coupled representation of benzenoid heterocyclic systems must now be regarded as a credible alternative to that from MO theory. In addition, there are now very good reasons to reconsider our attitudes to the classical VB descriptions of these systems.

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