The Electronic Structure of Heteroaromatic Molecules. Part 3.[3] A Comparison of Benzene, Borazine, and Boroxine

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Spin-coupled theory has been applied to the π electrons of the heteroaromatic molecules borazine and boroxine. Benzene is also reconsidered with more elaborate calculations than were used in previous work. The spin-coupled description of benzene, with semi-localized orbitals, is the same as that found previously. The close relationship between the spin-coupled wavefunctions and those from multiconfiguration SCF calculations is explored using large basis sets.

Marked differences are found between the spin-coupled descriptions of organic benzenoid systems and of these inorganic rings. Whereas the benzenoid aromatic molecules are stabilized by the mode of coupling the spins of the π electrons, this is not an important effect in borazine and boroxine.

The spin-coupled π orbitals for the boron heterocycles take the form of two distorted 2p orbitals on each nitrogen or oxygen atom. One orbital is very localized while the other shows very significant delocalization onto neighbouring boron centres. Any special stabilization of these two molecules must arise almost entirely from distortion effects in the orbitals. However, we find that borazine and boroxine are very similar, and we suggest that neither molecule has significant aromatic character.

Spin-coupled calculations have shown that the π-electron systems in benzene, pyridine, pyridazine, pyrimidine, pyrazine, pyrrole, furan, thiophene, and thiazole are much better described in terms of localized non-orthogonal orbitals than by self-consistent field (SCF) molecular-orbital theory.[1–3] The special stability of aromatic molecules such as these arises from the particular mode of coupling the spins of the π electrons rather than from any supposed delocalization of the orbitals. The differences between the spin-coupled and molecular-orbital (MO) descriptions arise mostly from the effects of electron correlation. In the present paper, we extend the spin-coupled description of heteroaromatic systems to borazine and boroxine. We also reconsider benzene with more elaborate calculations.

There now exists a vast amount of literature information on inorganic heterocycles and much of this has been reviewed in two recent volumes edited by Haiduc and Sowerby.[4] The most extensively studied of the boron–nitrogen heterocycles, and probably the system of most interest to organic chemists, is the six-membered ring borazine $B_3N_3H_6$ containing an alternating arrangement of B and N atoms. This molecule has frequently been termed 'inorganic benzene' because of the possibility of aromatic stabilization in the π-electron system. The six-membered ring boroxine $B_3O_3H_3$, with an alternating arrangement of B and O atoms, is of interest for much the same reason. In the gas phase, at least, borazine is fairly similar to benzene in terms of physical properties and structure. However, $B_3N_3H_6$ is much more reactive than C_6H_6 and readily undergoes addition reactions rather than electrophilic substitution.

Not surprisingly, there has been much speculation over the relationship between benzene, borazine, and boroxine. In particular, SCF MO calculations with rather modest basis sets have been used to discuss the electronic structures of these molecules.[5,6] All of these studies neglected the effects of electron correlation on the π-electron systems and thus compared the degree of delocalization of SCF MOs. We now believe that the motion of *correlated* electrons in organic heterocycles is much better described in terms of localized non-orthogonal orbitals, so it seems very worthwhile to examine these inorganic molecules in terms of spin-coupled theory.

Calculations.—All of our calculations for benzene, borazine, and boroxine utilized experimental geometries without regard to the error bars, except in the case of the angles in borazine. The structure of borazine has been investigated by electron diffraction techniques[7] and this molecule is believed to be planar with D_{3h} symmetry. The bond lengths thus determined are B–N 1.4355 ± 0.0021 Å, B–H 1.258 ± 0.14 Å and N–H 1.050 ± 0.012 Å. The ring angles are NBN 117.7 ± 1.2° and BNB 121.1 ± 1.2°. In order to produce a geometry with a closed planar ring, we assumed equal errors in the two angles and used NBN 118.3° and BNB 121.7°.

Boroxine is stable in the gas phase in the presence of a diluting inert gas, but disproportionates at room temperature in condensed phases to yield B_2O_3 and B_2H_6. The planar D_{3h} structure of $B_3O_3H_3$ has been confirmed by electron-diffraction studies in the gas phase[8] and the bond lengths were determined to be B–O 1.375 ± 0.002 Å and B–H 1.192 ± 0.017 Å, with angles of 120 ± 0.64°. For benzene (D_{6h}), we used bond lengths C–C 1.3964 Å and C–H 1.0831 Å, taken from vibration–rotation spectroscopy.[9]

Two separate series of calculations were performed. The first of these is completely analogous to the previous treatment of organic heterocycles.[2,3] The basis sets (B,C,N,O/H) of (10s 5p/4s) primitive Gaussians contracted to [3s 2p/2s] were taken directly from Dunning and Hay[10] and for each molecule we first carried out a standard SCF calculation at the geometry described above. We use the label DH for these basis sets.

Spin-coupled calculations were then performed for the six π electrons with the electrons of the σ framework accommodated in doubly occupied SCF molecular orbitals. The calculations

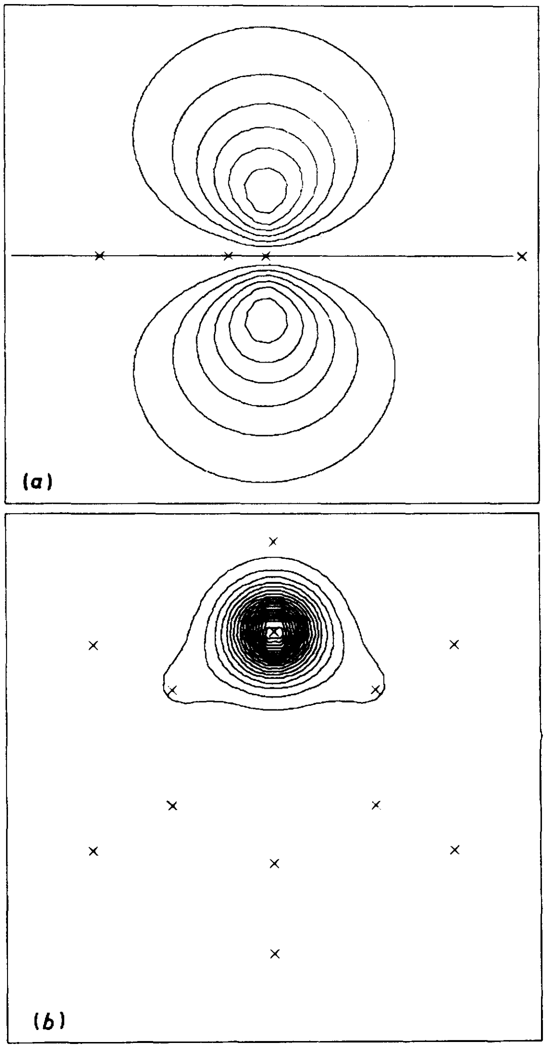

Figure 1. Spin-coupled orbital φ_1 in benzene (DH basis). Five other orbitals are related by symmetry to this one. Throughout this work we present contour plots of the square modulus of the orbitals, $|\varphi_\mu(r)|^2$. Orbital shown (*a*) at one of the C atoms in a σ_v mirror plane; (*b*) in the plane 1 bohr above the σ_h molecular plane.

utilize the complete spin space (five modes of spin coupling) and each of the six spin-coupled orbitals is allowed to overlap freely with each of the others.

The second series of calculations was rather more elaborate. First of all, much larger basis sets of triple-zeta plus polarization (TZVP) quality were used. The basis sets for (B,C,N,O/H) consisted of (10s 6p/5s) primitive Gaussians contracted to [5s 3p/3s][11] and were augmented with polarization functions with exponents $p_H = 1.0$, $d_B = 0.50$, $d_C = 0.72$, $d_N = 0.98$, and $d_O = 1.28$. Six components were used for the (Cartesian) d functions.

In addition to the use of large basis sets, a multiconfiguration SCF calculation was performed for each molecule. We refer to this method as the complete active space SCF (CASSCF) method because the wavefunctions include all 175 configurations which may be generated by distributing the six 'active' electrons in six orthogonal MOs. The doubly-occupied σ orbitals for the 'inactive' electrons were allowed to 'relax,' in a self-consistent manner, in the field of the improved description of the π electrons.

The CASSCF method leads to lower energies for these molecules than does SCF theory. This lowering arises from the inclusion of electron correlation effects for the π electrons, and also because of the slightly improved description of the σ 'core' in the presence of the correlated π-electron system. However, the interpretation of the configuration interaction (CI) coefficients for 175 configurations is not straightforward, particularly since a fair number of these have significant values. One alternative is known as the natural orbital description: instead of CI coefficients one must interpret fractional occupation numbers for the 'active' orbitals. For example, we find that the occupation numbers for the six π natural orbitals of borazine are 1.984, 1.976, 1.976, 0.027, 0.019, and 0.019. The significance of an occupation number of, say, 1.976 electrons is not transparent to most chemists, including the current authors.

Table 1. Total energies (in hartree) using the DH basis sets.

	Benzene	Borazine	Boroxine
SCF	−229.995 14	−241.079 70	−300.589 43
Spin-coupled	−230.070 97	−241.120 27	−300.634 51
Full-valence VB	−230.077 87	−241.120 70	−300.634 68
Structure R_1	−230.037 43	−241.119 91	−300.634 41

Table 2. Total energies (in hartee) using the TZVP basis sets.

	Benzene	Borazine	Boroxine
SCF	−230.770 35	−241.220 45	−300.798 21
Spin-coupled	−230.835 13	−241.260 11	−300.842 73
CASSCF-175	−230.842 66	−241.260 45	−300.842 84

Spin-coupled calculations were then carried out with the electrons of the σ framework accommodated in the doubly occupied 'inactive' CASSCF orbitals. As before, the spin-coupled calculations involved the six π electrons, which were expanded in all the basis functions of π symmetry.

Results

The first observation, for each molecule, is that we do not find any major differences between the spin-coupled orbitals from the two series of calculations. For benzene, there are six equivalent spin-coupled π orbitals which are transformed into one another by successive $\hat{C}_6$ rotations. One of the orbitals is shown in Figure 1 as contour plots of $|\varphi_1|^2$ in a σ_v mirror plane (at a C atom) and in the plane one unit of atomic distance (1 bohr, *ca.* 5.3×10^{-11}m) above the σ_h molecular plane. Each of the orbitals closely resembles a C(2p) function, perpendicular to the ring, but is distorted symmetrically towards the carbon atoms on either side. The spin-coupled wavefunction provides an improvement over the SCF energy by 199 kJ mol^{-1} in the DH basis and by 170 kJ mol^{-1} in the TZVP basis. Energies are collected in Tables 1 and 2, and the overlaps between the orbitals in Table 3.

The distortion of the spin-coupled orbitals for benzene occurs because of the small amount of ionic character needed to describe the C–C π bonds. Ionic structures in spin-coupled theory are those in which one or more of the orbitals is allowed to be doubly occupied. Allowing for the different numbers of allowed spin functions, and including the spin-coupled configuration, a total of 175 VB structures can be generated in this way. A non-orthogonal CI calculation with the DH basis using these 175 structures (a 'full-valence VB') gives a further energy lowering of 18 kJ mol^{-1}. The relative magnitude of this figure suggests that the small distortion effects in the spin-coupled orbitals, which are no larger than those we have seen for the C–C π bonds in alkenes, already take into account the most important of the ionic effects. The same would not be true in classical VB theory where ionic structures would be essential,

Table 3. Overlap integrals between spin-coupled orbitals (TZVP basis sets) for benzene, borazine, and boroxine.

	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
			Benzene			
φ_1	1	0.52	0.03	−0.16	0.03	0.52
φ_2		1	0.52	0.03	−0.16	0.03
φ_3			1	0.52	0.03	−0.16
φ_4				1	0.52	0.03
φ_5					1	0.52
φ_6						1
			Borazine			
φ_1	1	0.81	0.07	0.13	0.07	0.13
φ_2		1	0.13	0.25	0.13	0.25
φ_3			1	0.81	0.07	0.13
φ_4				1	0.13	0.25
φ_5					1	0.81
φ_6						1
			Boroxine			
φ_1	1	0.82	0.05	0.10	0.05	0.10
φ_2		1	0.10	0.22	0.10	0.22
φ_3			1	0.82	0.05	0.10
φ_4				1	0.10	0.22
φ_5					1	0.82
φ_6						1

Table 4. Occupation numbers of the Rumer spin functions, expressed as percentages (DH basis sets).

	R_1	R_2	R_3	R_4	R_5
Benzene	40	6.5	6.5	40	6.5
Borazine	91	3	3	0	3
Boroxine	95.5	1.5	1.5	0	1.5

because of the use of strictly localized orbitals. The spin-coupled configuration is overwhelmingly dominant in the full-valence VB wavefunction and so we can claim with confidence that the inclusion of spin-coupled ionic structures does not change the essential physical picture.

We have not carried out a full-valence VB calculation with the TZVP basis set, as it should produce exactly the same energy as the 175-configuration CASSCF wavefunction. For a system with N electrons, a spin-coupled calculation followed by a full-valence VB is formally equivalent to a CASSCF description with all allowed distribution of N electrons in N orthogonal orbitals. Robb and co-workers[12] have shown how in principle one might transform between these two descriptions. Although the two wavefunctions have the same number of structures, the ease of interpretation is very different in the two cases.

The spin-coupled calculations correspond to an expansion in the complete spin space (five functions for six electrons with a net spin of zero). For a discussion of different spin functions, and of the relationships between them, see *e.g.* ref. 13. All the spin-coupled calculations were carried out using the Kotani basis of spin functions. As in our previous work on organic ring systems,[1–3] we also transformed our wavefunction into the more familiar basis of Rumer functions which is used in classical VB theory. Note that this transformation affects only the weights of the spin functions—it does not modify the orbitals.

For benzene, with the orbitals ordered φ_1 to φ_6 around the ring, Rumer functions R_1 and R_4 correspond to Kekulé-type structures, whereas the others correspond to *para*-bonded or Dewar-type structures. As shown in Table 4, we find weights of *ca.* 40% for each of R_1 and R_4, and *ca.* 6.5% for each of the others. For definitions of the different Rumer structures, see ref. 2 (particularly Figure 4). The energy of the dominant structure (R_1) is given in Table 1. The difference between this energy and that derived from a calculation with all five Rumer structures can reasonably be termed the resonance energy. In this way, we obtain a value of 88 kJ mol^{-1} in the DH basis. If we allow also for the spin-coupled ionic structures, this value is increased to 106 kJ mol^{-1}.

We turn next to the spin-coupled description of the six π electrons in borazine. At first sight, there are marked similarities to benzene. The spin-coupled wavefunction corresponds to energies which are 107 kJ mol^{-1} (DH basis) and 104 kJ mol^{-1} (TZVP basis) lower than those from the SCF calculations. We find that the spin-coupled ionic structures are even less important (*ca.* 1 kJ mol^{-1}) than was the case for benzene. Three of the spin-coupled orbitals are related to each other by successive $\hat{C}_3$ rotations and they take the form of fairly localized, slightly distorted N(2p) functions. The other three orbitals are also transformed into one another by successive $\hat{C}_3$ operations. These are also based on N(2p) functions but clearly show considerable delocalization onto neighbouring boron centres. Nonetheless, most of the density remains on N.

Starting at one of the N atoms, and proceeding around the ring, we refer to the more localized orbitals as φ_1, φ_3, and φ_5, and to the less localized orbitals as φ_2, φ_4, and φ_6. Orbitals φ_1 and φ_2 are shown in Figure 2 as contour plots of $|\varphi_\mu|^2$. The top row of views corresponds to a σ_v mirror plane (at one of the N atoms), while the bottom row relates to the plane one unit of atomic distance above the σ_h molecular plane. Despite the large difference in the degree of delocalization onto B atoms, the overlap between φ_1 and φ_2 is 0.813 (see Table 3).

The differences from the organic rings become more apparent when we examine the weights of the different spin functions in the Rumer basis (see Table 4). In this case, structure R_1 corresponds to singlet coupling of the two electrons in the orbitals associated with each N atom. The other functions contribute a total of only 9%, and the difference in energy between structure R_1 and the full calculation is very small. Using the same definition of resonance energy as before, we obtain an almost negligible value.

A very similar situation arises for boroxine. Orbitals φ_1, φ_3, and φ_5 are fairly localized functions on oxygen, but orbitals φ_2, φ_4, and φ_6 show delocalization onto neighbouring B centres. The orbitals in each set are related to one another by symmetry, as before. Contour plots for orbitals φ_1 and φ_2 are shown in Figure 3. It can be seen that the delocalization is smaller than was the case for borazine, although the overlap between orbitals φ_1 and φ_2 is only slightly larger (0.823). In this case, structure R_1 contributes 95.5% of the spin-coupled wavefunction, and the resonance energy, defined as before, is negligible.

The improvement of the spin-coupled energies over those from the SCF calculations is slightly larger than for borazine (118 kJ mol^{-1} in the DH basis and 117 kJ mol^{-1} in the TZVP basis). Spin-coupled ionic structures are even less important than for borazine. One consequence of this is that the spin-coupled calculation with the TZVP basis gives an energy only 10^{-4} hartree higher than a 175-configuration CASSCF description. We have already commented on the vastly different ease of interpretation of these two wavefunctions.

Estimates of the conjugation energies for these molecules vary significantly, depending on the particular definition that is adopted. For a molecule $X_nY_lH_m$, an isodesmic reaction is one in which the number of XX, XY, XH, and YH linkages is conserved. Using rather limited basis sets at the SCF level, Haddon[5] considered the isodesmic reactions:

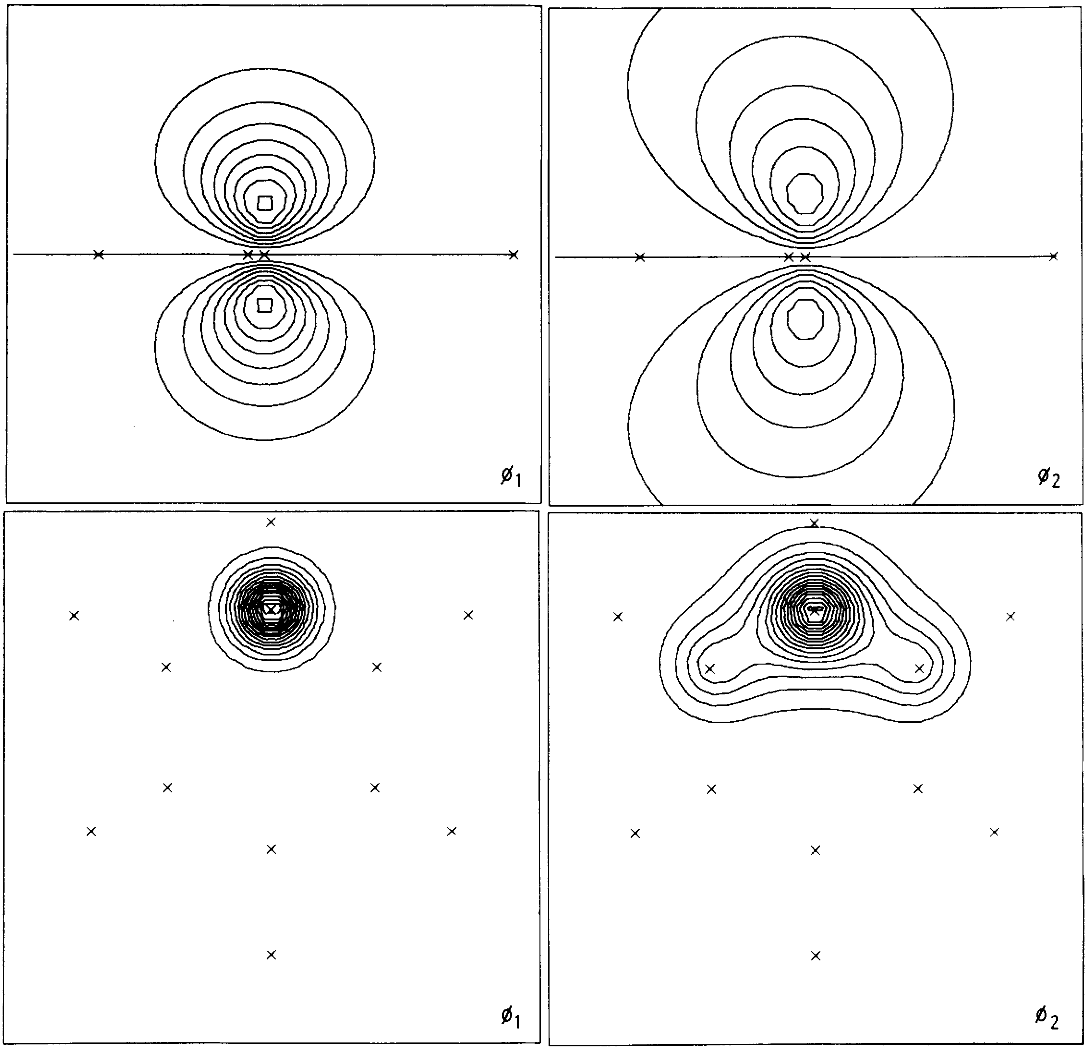

Figure 2. Spin-coupled orbitals φ_1 and φ_2 in borazine (DH basis). Two other orbitals are related by symmetry to each of these. Top row: at one of the N atoms in a σ_v mirror plane. Bottom row: in the plane 1 bohr above the σ_h molecular plane.

$$\begin{aligned} C_6H_6 + 6\ CH_4 &\longrightarrow 3\ CH_2CH_2 + 3\ CH_3CH_3 \\ B_3N_3H_6 + 3\ BH_3 + 3\ NH_3 &\longrightarrow 6\ BH_2NH_2 \\ B_3O_3H_3 + 3\ BH_3 + 3\ H_2O &\longrightarrow 6\ BH_2OH \end{aligned}$$

and found a positive conjugation energy for benzene, but negative values for both borazine and boroxine. Using a different approach, but still at the SCF level and in a minimal basis set, Cao and Wang[14] have also found negative conjugation energies for these inorganic rings. Rather different values come from considerations of homodesmotic reactions, which aim to conserve the number of XX, XY, and YY bonds of each type, as well as the number of H atoms attached to each X or Y atom. From the homodesmotic reactions:

$$\begin{aligned} C_6H_6 + 3\ CH_2{=}CH_2 &\longrightarrow 3\ CH_2{=}CH{-}CH{=}CH_2 \\ B_3N_3H_6 + 3\ BH_2NH_2 &\longrightarrow 3\ BH_2{-}NH{-}BH{-}NH_2 \\ B_3O_3H_3 + 3\ BH_2OH &\longrightarrow 3\ BH_2{-}O{-}BH{-}OH \end{aligned}$$

Haddon[5] proposed that the conjugation energy for borazine is positive and roughly one third of that for benzene, but that the value for boroxine is essentially zero.

If borazine does have a positive conjugation energy, then it is clear from our calculations that we cannot attribute much of this stabilization to the mode of spin coupling, as was the case for the organic rings. In our model, such stabilization as there is must arise from the very significant delocalization effects seen in some of the orbitals. Unfortunately, it is rather difficult to estimate the contributions that these distortions make to the total energy. In molecules at equilibrium geometry, we always find that the spin-coupled orbitals show some degree of deformation from purely localized forms—it is simply that the effects are much larger in these inorganic rings.

By restricting the coefficients of basis functions on neighbouring B atoms, we have artificially modified orbitals φ_2, φ_4, and φ_6 in borazine and boroxine so as to reduce the overlap between them. This procedure is somewhat arbitrary, and depending on how much we modify the orbitals we can obtain almost any energy change we like. However, we do find that the changes for borazine are only slightly larger than those for boroxine. Thus, we are currently unable to rationalize the difference in conjugation energies expected from theoretical considerations of homodesmotic reactions.[5]

None of the spin-coupled orbitals for the six-membered organic heterocycles in previous work showed any degree of deformation that was out of the ordinary.[2] However, for the five-membered rings with two orbitals on the same heteroatom, one of these orbitals clearly showed some delocalization onto neighbouring carbon centres.[3] This was most dramatic for the sulphur atoms in thiophene and thiazole. If the distortion effects

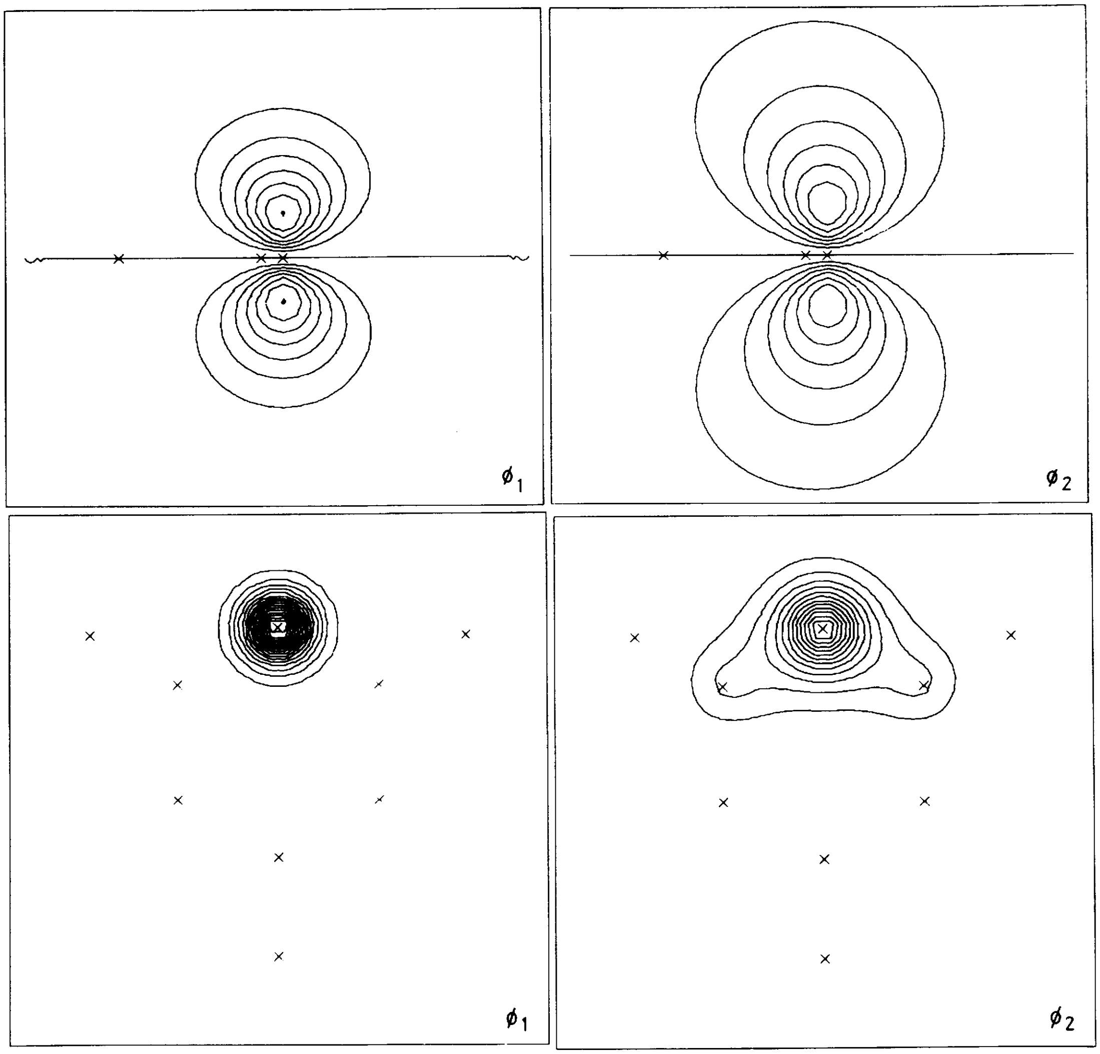

Figure 3. Spin-coupled orbitals φ_1 and φ_2 in boroxine (DH basis). Two other orbitals are related by symmetry to each of these. Top row: at one of the O atoms in a σ_v mirror plane. Bottom row: in the plane 1 bohr above the σ_h molecular plane.

do indeed result in a favourable conjugation energy for borazine, then it is possible that our estimates of stabilization energies for the sulphur heterocycles, based only on the mode of spin coupling, might have been underestimates. However, we consider it more likely that neither borazine nor boroxine has any significant aromatic character.

Finally, we consider very briefly the effects of electron correlation on the total electron densities from the SCF and the spin-coupled (or CASSCF) descriptions. Although the SCF and spin-coupled orbital pictures of benzene are very different, the total electron densities are fairly similar. However, as is to be expected, the SCF description exaggerates the extent of charge accumulation in the internuclear regions. We have also examined the SCF and spin-coupled total electron densities for pyridine[2] using a modification of the topological partitioning scheme developed by Bader and co-workers.[15] The electron correlation taken into account by the spin-coupled method increases slightly the covalency of the π bonds.[16]

Conclusions

This study shows that the correlated π electrons in borazine and boroxine are much better described in terms of non-orthogonal semi-localized orbitals than they are by the delocalized orthogonal MOs of SCF theory. In this sense, there are similarities with the spin-coupled descriptions of the organic heterocycles considered previously.[2,3] However, there are also very significant differences. Whereas the characteristic stability of organic aromatic molecules such as benzene is a direct consequence of the mode of spin coupling, this is not an important effect in borazine or boroxine.

The spin-coupled π orbitals for borazine and boroxine take the form of two distorted 2p orbitals on each nitrogen or oxygen atom. One of the orbitals on each of these atoms is very localized, while the other shows very significant delocalization onto the neighbouring boron centres. Any special stabilization of these two molecules must arise almost entirely from the distortion effects in the orbitals. Structure R_1 is less dominant and the orbital distortion effects are larger for borazine than for boroxine. However, we have not been able to show a significantly larger energy stabilization for borazine than for boroxine.

Aromaticity is a rather vague concept that has proved to be of great utility at a qualitative level. However, it is very difficult to present clear experimental or theoretical criteria for distinguishing between aromatic and non-aromatic molecules.[17] Certainly, experimental energy differences are not conclusive, particularly as different reaction schemes can produce widely differing estimates of stabilization energies. It is also hard to produce convincing chemical criteria. Nonetheless, we believe that it is fair to say that there is very little evidence for the supposed aromaticity of borazine. Although this molecule is similar to benzene in terms of physical properties and structure, it is much more reactive and readily undergoes addition reactions rather than electrophilic substitution. Except for theoretical considerations of homodesmotic reactions using small basis sets at the SCF level, there is little reason to consider that borazine has any unexpected stability. The spin-coupled calculations for borazine and boroxine appear to suggest that neither molecule has any significant aromatic character.

The close relationship between the spin-coupled wavefunction and certain CASSCF wavefunctions has been demonstrated using large basis sets. The spin-coupled wavefunction for each of these systems turns out to be very similar to that from a CASSCF calculation with all allowed distributions of six electrons in six orthogonal π MOs (175 configurations). The very small differences in energy between these two descriptions are due to the contributions from structures in which one or more spin-coupled orbitals is allowed to be doubly occupied. Of course, the spin-coupled wavefunction, with just one spatial configuration, is very much easier to interpret.

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