The Electronic Structure of 1,3-Dipoles: Hypervalent Atoms

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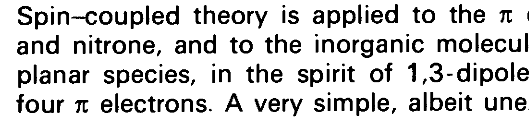
Spin–coupled theory is applied to the π electrons of the 1,3-dipoles diazomethane, fulminic acid, and nitrone, and to the inorganic molecules O_3, N_2O, and NO_2. The linear molecules are treated as planar species, in the spirit of 1,3-dipoles taking part in cycloaddition reactions as systems with four π electrons. A very simple, albeit unexpected picture arises for the bonding in these π-electron systems. The central nitrogen atom in CH_2N_2, for example, takes part in *five* covalent bonds. We use the label 'hypervalent' for such a situation, and we identify hypervalent atoms in all of the molecules considered. We discuss the consequences of our model for the chemistry and properties of 1,3-dipoles.

It is generally accepted that 1,3-dipolar cycloaddition reactions involve four 'π' electrons from the 1,3-dipole and two from the dipolarophile. Examples of 1,3-dipoles include fulminic acid, diazoalkanes, nitrones, and carbonyl ylides. We might reasonably add to this list the inorganic molecules nitrous oxide and ozone. The dipolarophile is typically a substituted ethene. Reviews of 1,3-dipolar cycloaddition chemistry are available from the two volumes edited by Padwa.[1]

A characteristic feature of this class of molecules is that it presents awkward problems for classical valency theories. The usual fashion of representing diazomethane, for example, involves resonance between a number of zwitterionic and diradical structures:



Various theoretical studies have stressed the importance of the diradical structure, but they also suggest non-negligible contributions from most of the other canonical structures.[2–5] All in all, the situation is very confused, with widely differing estimates of the relative weights of the different bonding schemes.

The very short bond lengths between the heavy atoms in CH_2N_2 appear to suggest fully-formed C=N and N≡N multiple bonds. Similarly, the experimental bond lengths in N_2O are very close to the values expected for an N≡N triple bond and an N=O double bond, so that it is tempting to represent this molecule as N≡N=O. According to Pauling,[6] 'this formula suggests that the nitrogen atom can form five covalent bonds, which is not true.' Nonetheless, there have been several attempts to explain how a nitrogen atom might acquire an apparent valency of five, including suggestions of resonance between 'increased-valence' structures[7] built from undistorted atomic orbitals. More recently, Kahn, Hehre, and Pople[8] compared the bond lengths of 1,3-dipoles with those of diatomic species, and commented that many of these molecules might appropriately be described in terms of structures with a 'hypervalent nitrogen atom,' but there were no suggestions as to how this might arise.

Calculations based on molecular orbital theory do little to clarify the interpretation of the bonding in these molecules. Closed-shell, restricted Hartree–Fock (RHF) calculations are not very convincing for the π electrons of 1,3-dipoles. Although unrestricted Hartree–Fock (UHF) calculations have been used with some success in geometry optimizations[8] and even in frontier orbital theory arguments, realistic descriptions of these molecules within the framework of molecular orbital theory generally require multiconfiguration wavefunctions.

In the current work we present a very simple, albeit rather unexpected, physical picture of the chemical bonding in 1,3-dipoles. As our examples we consider fulminic acid (HCNO), nitrone (CH_2NHO), and diazomethane (CH_2N_2), as well as the triatomics N_2O, O_3, and NO_2. Because of the nature of 1,3-dipolar cycloaddition reactions, we have concentrated our attention on the four π electrons—in the case of the linear molecules HCNO and N_2O, we arbitrarily selected one of the planes containing the internuclear axes. The NO_2 radical reacts rather differently from the other molecules, because of the unpaired electron, but its structure poses very similar problems for classical valency theories.

Our description of the π electrons in these systems is based on spin–coupled theory. The general approach is very similar to that used recently for heteroaromatic molecules,[9–11] for which it was argued that the π-electron systems are very much better described in terms of localized non-orthogonal orbitals than by the delocalized orthogonal orbitals of Hartree–Fock (molecular orbital) theory. Our representation of the bonding in 1,3-dipoles turns out to be even more novel. We demonstrate, for example, that the nitrogen atom in diazomethane takes part in *five* fairly normal two-electron covalent bonds. We use the label 'hypervalent' for such a situation.

We present clear theoretical evidence for hypervalent atoms in all six molecules considered. We discuss our findings in terms of the properties and reactivity of 1,3-dipoles and we comment on the probable significance of our findings for understanding the chemistry of explosives.

Spin-coupled Theory.—We start with a very brief overview of those qualitative features of spin-coupled theory which are of particular importance to the present study. Details of the theory and of its computational implementation have been published in several places and at several levels, including an extensive specialist review.[12] Useful introductions for the non-theoretician include our recent papers on benzenoid heterocycles[9–11] and a general review.[13]

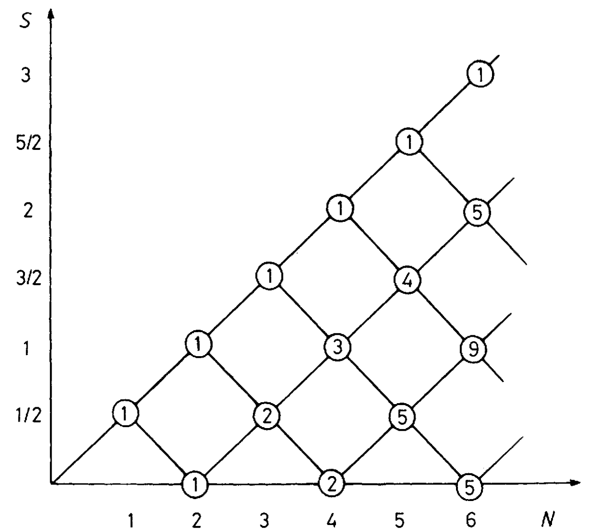


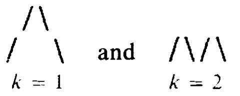
Figure 1. Branching diagram for up to six electrons.

In general, the spin-coupled wavefunction is based on an orbital picture with one orbital for each electron, and with no orthogonality requirements of any kind. Spin-coupled theory differs from classical valence bond (VB) approaches in that the orbitals are not constrained to be purely localized around particular nuclei. Instead, the orbitals are fully optimized in the form of linear combinations of basis functions drawn from all the atomic centres, much as in MO theory. The form of the orbitals is a unique outcome of the variational procedure, and these are as localized or as delocalized as is necessary to achieve the lowest energy. For most molecules, it turns out that the orbitals are all distinct and resemble slightly deformed classical VB orbitals. All of the orbitals overlap with one another.

One important consequence of the use of non-orthogonal orbitals is that there is usually more than one way of coupling together the spins of the individual electrons so as to produce the required total spin. Spin-coupled calculations are usually performed using an expansion in the complete spin space. This turns out to be particularly important when considering the breaking of old bonds and the making of new ones in a chemical reaction.

The spin-coupled description may be refined subsequently in a non-orthogonal configuration interaction calculation. This also allows us to provide highly accurate descriptions of excited states. Further details are given in the reviews cited above. An important result, from all of our work to date, is that the final wavefunction for the ground state is always dominated by the spin-coupled configuration for all nuclear geometries. Consequently, we may claim that the further refinement of the spin-coupled wavefunction, which is based on just one spatial configuration, does not change the essential physical picture. Our method combines high accuracy with ease of interpretation.

The calculations in the present work used the Kotani basis of spin functions. For a discussion of different spin functions, and of the relationships between them, see the book by Pauncz,[14] for example. The Kotani functions may be visualized easily in terms of the branching diagram (Figure 1), where the axes show the total spin S for various numbers of electrons N. The electron spins are coupled together one at a time, according to the usual rules for combining angular momenta, such that each partial spin function is an eigenfunction of $\hat{S}^2$ (and of $\hat{S}_z$). The different linearly-independent spin functions correspond to different rightward paths on the diagram, with the numbers in the circles denoting the total number of routes to each point. In particular, for $N = 4$ and $S = 0$, the complete spin space consists of just two spin functions:



where the function labelled $k = 2$ is known as the perfect-pairing spin function. It corresponds exactly to the perfect-pairing Rumer function, in which the first two electrons have opposite spin and similarly the last two electrons.

Spin-coupled Calculations on 1,3-*Dipoles*.—The molecules considered in this work are drawn in Figure 2, in order to establish a convention for labelling the nuclei, to define the orientation of the molecules in later figures, and to report the geometries employed. All the bond lengths and angles were taken from a standard compilation of experimental data[15] or from previous theoretical work, in the case of nitrone.[16]

We used basis sets (C, N, O/H) of (10s 6p/5s) primitive Gaussians contracted to [5s 3p/3s].[17] The exponents used for hydrogen were 33.64, 5.058, 1.147, 0.3211, and 0.1013. These basis sets of approximately triple-zeta quality were augmented with polarization functions with exponents $d_C = 0.72$, $d_N = 0.98$, $d_O = 1.28$, and $p_H = 1.0$. We use the label TZVP for these basis sets. Five components were used for the (spherical) d functions. A preliminary account of calculations on nitrone with a TZVP basis set and on diazomethane with a somewhat smaller basis set has already been published.[18]

For each of CH_2N_2, HCNO, CH_2NHO, N_2O, and O_3 we first performed a standard RHF self-consistent field (SCF) calculation. Spin-coupled calculations were then carried out for the four π electrons, with the electrons of the σ framework accommodated in the corresponding SCF molecular orbitals (MOs). For diazomethane, a slightly more sophisticated calculation was also performed. This is equivalent to allowing the MOs for the σ electrons to relax, in a self-consistent manner, in the field of the correlated π electrons. Exactly how this is achieved will be described later, but it is important to mention now that we find that this improved description of the σ 'core' has a negligible effect on the spin-coupled description of the π electrons.

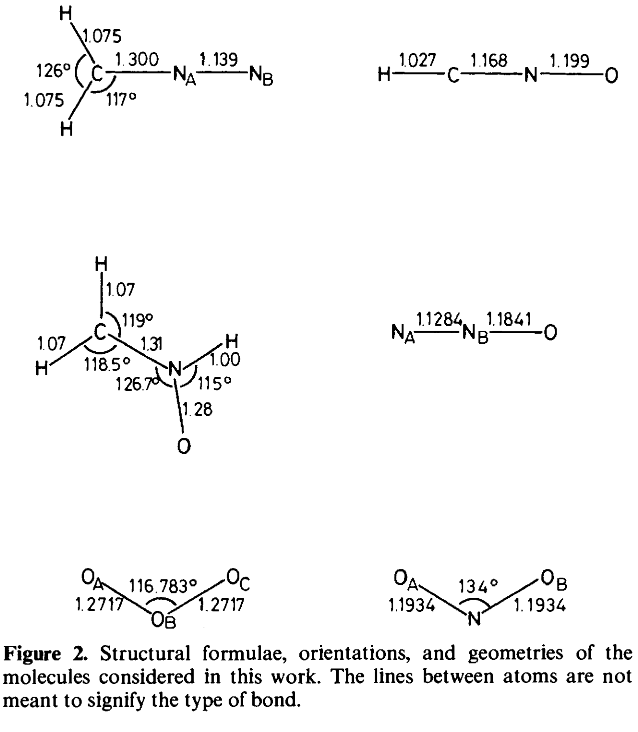


Figure 2. Structural formulae, orientations, and geometries of the molecules considered in this work. The lines between atoms are not meant to signify the type of bond.

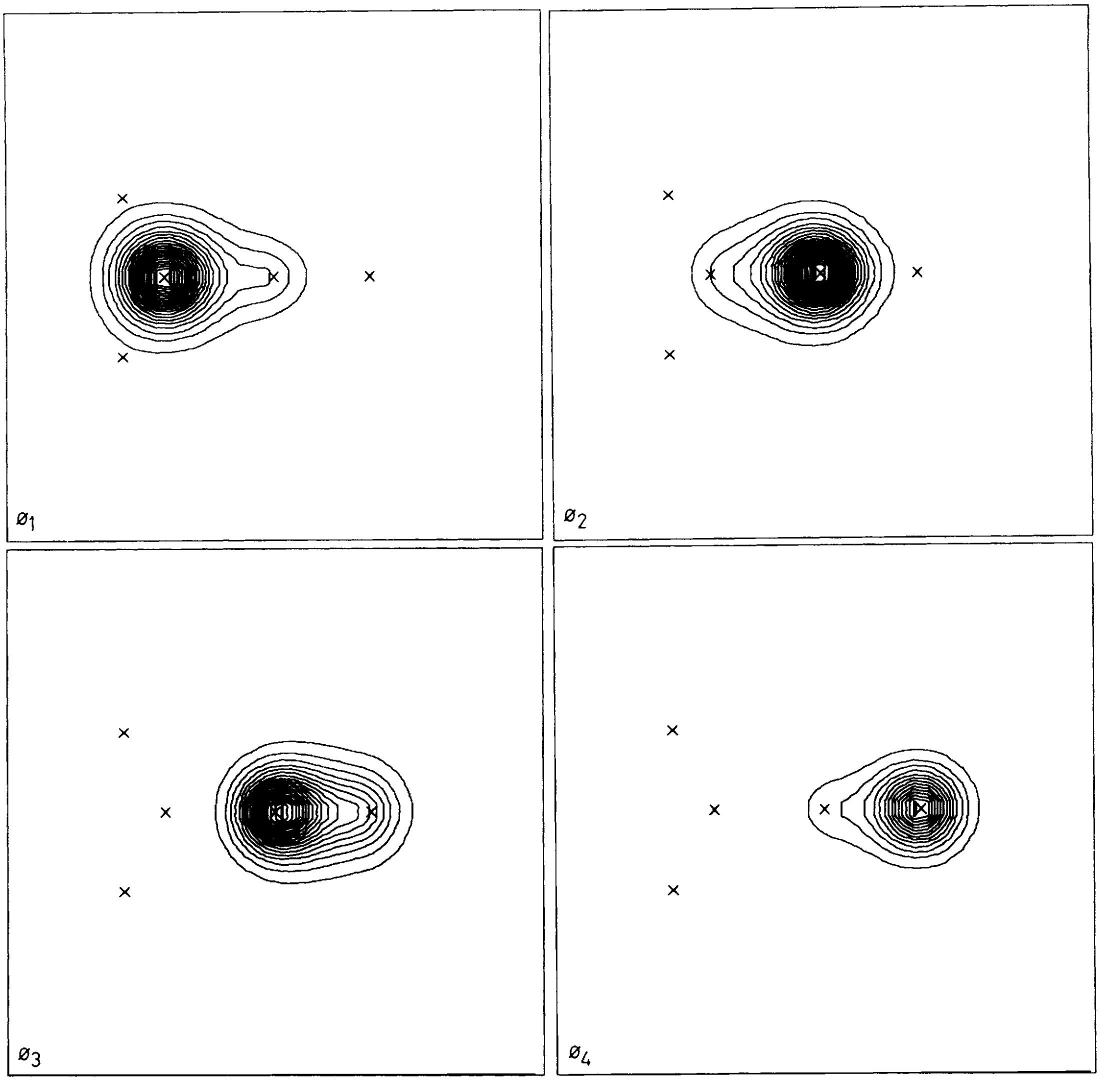


Figure 3. Contour plots for CH_2N_2 of the square modulus of the spin-coupled orbitals, $|\varphi_\mu(r)|^2$, in the plane 1 bohr above the molecular plane (σ_v' mirror). The positions of the nuclei, in the plane below, are marked with crosses.

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

	SCF	Spin-coupled	Full-valence VB
CH_2N_2	−147.890 22	−147.932 11	−147.932 39
HCNO	−167.683 11	−167.725 70	−167.726 16
CH_2NHO	−168.870 08	−168.923 44	−168.923 99
N_2O	−183.735 19	−183.782 26	−183.782 70
O_3	−224.327 67	−224.427 37	−224.427 66
NO_2	−204.088 34	−204.140 72	−204.140 83[a]

[a] Spin-coupled ionic configurations were included only for the four π electrons.

The spin-coupled calculations for the four π electrons involved both spin functions for $N = 4$ and $S = 0$, and each of the four spin-coupled orbitals was allowed to overlap freely with each of the others. However, the orbitals were constrained only to use basis functions of π symmetry (*i.e.* those which are antisymmetric with respect to reflection in the molecular plane).

Because of the unpaired electron, NO_2 was treated slightly differently from the other molecules. We first performed an open-shell RHF calculation for this molecule. Spin-coupled calculations were then carried out for *five* electrons with the 18 electrons of the σ 'core' (a_1 and b_2 symmetry in the C_{2v} point group) accommodated in doubly occupied RHF MOs. The five spin-coupled orbitals were expanded in a basis comprising the singly occupied RHF MO and all the unoccupied MOs of σ or π symmetry. This is equivalent to optimizing the five spin-coupled orbitals as completely general linear combinations of *all* the atomic basis functions, except that each orbital is constrained to be orthogonal to those in the σ core. This restriction is necessary to prevent violation of the Pauli principle. No further symmetry or orthogonality requirements were imposed on the spin-coupled orbitals, and we included all five spin functions for $N = 5$ and $S = \frac{1}{2}$. There were no symmetry constraints on the total wavefunction, but the converged solution was found to correspond to a $^2A_1$ state, as it should.

Results

Diazomethane.—For CH_2N_2, the spin-coupled description of the four π-electrons gives an energy which is significantly lower than that given by the SCF calculation (see Table 1). This improvement in the total energy of 110 kJ mol^{-1} arises from the effects of electron correlation. The spin-coupled orbitals φ_μ are

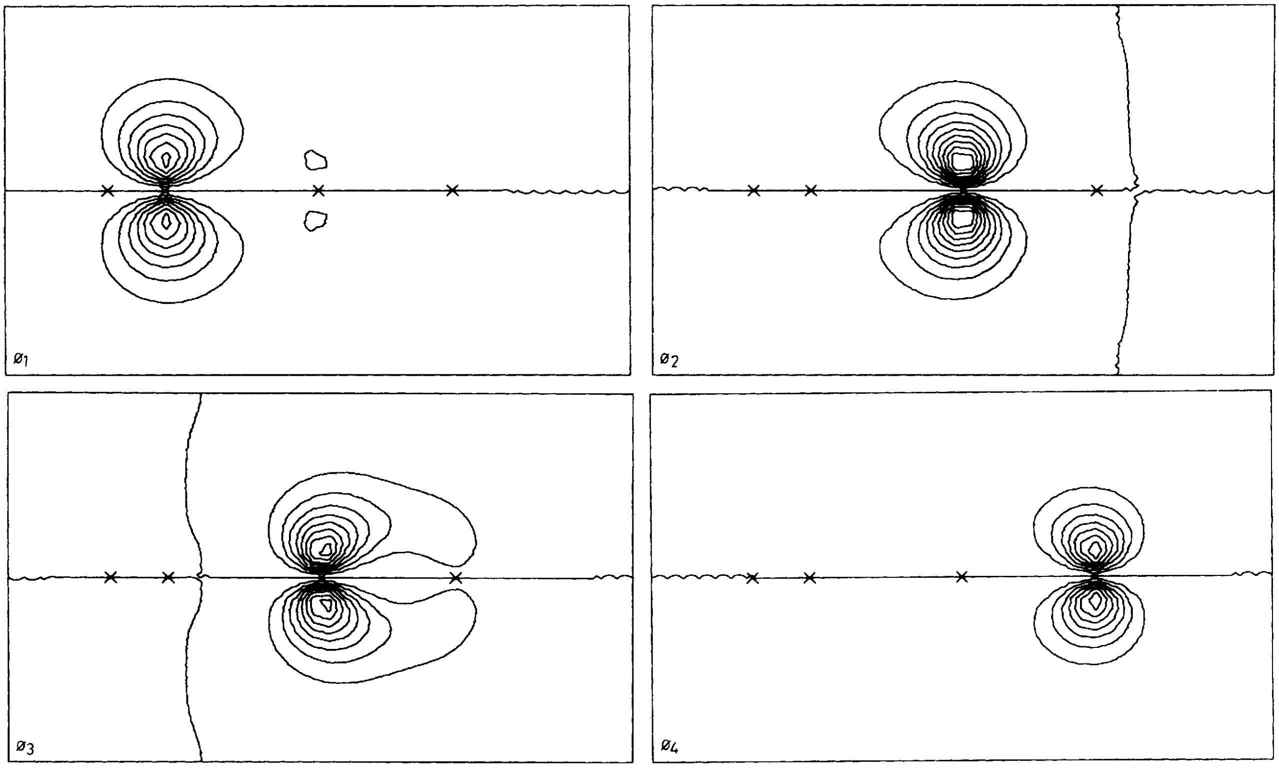


Figure 4. Contour plots for CH_2N_2 of $|\varphi_\mu(r)|^2$ in the σ_v mirror plane perpendicular to the molecular plane. The positions of the nuclei, projected onto this plane, are marked with crosses.

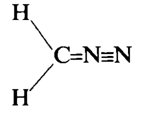
shown as contour plots in two different planes in Figures 3 and 4. Throughout this work, we plot $|\varphi_\mu(r)|^2$ in a plane one unit of atomic distance (1 bohr $\approx 5.3 \times 10^{-11}$ m) above the molecular plane and, whenever the molecule has a linear heavy-atom backbone, in the mirror plane perpendicular to the molecular plane and containing the heavy atoms.

Each of the spin-coupled orbitals in CH_2N_2 takes the form of a $2p_x$ function pointing perpendicular to the molecular plane. The overlap integrals between the orbitals are reported in Table 2. Orbital φ_1 is essentially localized on C, but is distorted towards N_A. Orbitals φ_2 and φ_3 are both based on 2p functions on N_A but are deformed in very different ways: φ_2 is distorted towards C but φ_3 shows significant distortion towards N_B. Finally, orbital φ_4 is essentially localized on N_B but shows some distortion towards N_A.

None of this appears to be particularly surprising until we examine the coefficients of the two spin functions. We refer to these as the spin-coupling coefficients c_{Sk} and, because the Kotani functions are orthonormal, the weights of the different modes of spin coupling are given by $|c_{Sk}|^2$. For diazomethane, the coefficient of the perfect-pairing spin function, with the orbitals ordered as described above, is $c_{02} = 0.995$ (*i.e.* 98.9% of the wavefunction). In other words, the bonding of the four π electrons in CH_2N_2 is dominated by that mode of spin coupling which corresponds to C–N and N–N π-bonds, with only a very small contribution from the corresponding diradical form.

Although orbitals φ_2 and φ_3 have an overlap of 0.785, the associated electron spins are not singlet-coupled as one might expect. One of the effects of electron correlation is to allow the two orbitals on the central nitrogen atom (N_A) to split and to couple instead to orbitals on the adjacent centres. We note that our previous calculations, in a smaller basis set without polarization functions, actually *underestimated* the magnitude of this effect.[18]

We include now the bonding in the σ framework—single bonds between C and N_A, and between N_A and N_B, and a further bond between N_A and N_B from the overlap of $2p_y$ atomic orbitals. The significance of our results for the π-electron system is now clear: the molecule has fully-formed $C{=}N_A$ and $N_A{\equiv}N_B$ bonds, so that the central nitrogen atom is hypervalent and takes part in *five* two-electron covalent bonds. It is perfectly reasonable to represent this molecule with the structure



although it is very important to clarify the meaning of the lines we have drawn between the atoms. The notation A-B signifies that there is one spin-coupled orbital essentially localized on A and another one on B; these two orbitals have a significant overlap, and the electron spins associated with them are coupled to a singlet. This description of the bonding is consistent with the observed NN bond length of 1.14 Å, which is very similar to that of isolated N_2 (1.10 Å). For comparison, the corresponding bond length in N_2O is 1.13 Å. Our picture of the bonding in CH_2N_2 is also consistent with the relatively small dipole moment of 1.45 D.[18,19]

One of the more unfortunate characteristics of classical VB methods, with purely localized orbitals, is the proliferation of significant contributions from ionic structures, even in predominantly covalent situations. Ionic configurations in spin-coupled theory are those in which one or more orbitals is doubly occupied. Including the spin-coupled configuration, and allowing for the different modes of spin coupling, a total of twenty VB structures can be constructed in this way from orbitals φ_1, φ_2, φ_3, and φ_4. We refer to a non-orthogonal configuration interaction calculation based on these twenty structures as a 'full-valence VB' calculation. The full-valence VB energy for diazomethane is quoted in Table 1—the further

Table 2. Overlap integrals between spin-coupled orbitals.

CH_2N_2	φ_1	φ_2	φ_3	φ_4	
φ_1	1	0.71	0.31	−0.30	
φ_2		1	0.78	−0.45	
φ_3			1	−0.79	
φ_4				1	
HCNO	φ_1	φ_2	φ_3	φ_4	
φ_1	1	0.70	0.06	−0.16	
φ_2		1	0.44	−0.26	
φ_3			1	−0.83	
φ_4				1	
CH_2NHO	φ_1	φ_2	φ_3	φ_4	
φ_1	1	0.64	0.07	0.20	
φ_2		1	0.51	0.27	
φ_3			1	0.79	
φ_4				1	
N_2O	φ_1	φ_2	φ_3	φ_4	
φ_1	1	0.69	0.09	0.16	
φ_2		1	0.49	0.27	
φ_3			1	0.83	
φ_4				1	
O_3	φ_1	φ_2	φ_3	φ_4	
φ_1	1	0.60	0.23	0.19	
φ_2		1	0.82	0.23	
φ_3			1	0.60	
φ_4				1	
NO_2	φ_1	φ_2	φ_3	φ_4	φ_5
φ_1	1	0.73	0.18	0.14	0
φ_2		1	0.59	0.18	0
φ_3			1	0.73	0
φ_4				1	0
φ_5					1

Table 3. Energies for diazomethane calculated using the TZVP basis set (with six d components). Further details are given in the text.

	Energy/hartree
SCF	−147.890 41
Spin-coupled	−147.932 66
CASSCF	−147.933 00

lowering over the spin-coupled energy is 0.7 kJ mol^{-1}. This suggests that the small amount of delocalization in the spin-coupled orbitals already accounts for all the important effects of ionic character—the addition of ionic structures is not then necessary.

The full-valence VB wavefunction for a system with N electrons is formally the same as that from a multiconfiguration self-consistent field calculation with all allowed distributions of N electrons in N orthogonal orbitals. This multiconfiguration wavefunction is usually denoted CASSCF (complete active space SCF). The equivalence between the full-valence VB and CASSCF wavefunctions only holds, of course, if exactly the same description is used for any 'inactive' or core electrons. Robb and co-workers[20] 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.

CASSCF calculations were performed for diazomethane with four active electrons and four active orbitals (twenty configurations). The geometry and TZVP basis set were precisely as described above, except that we used cartesian Gaussian functions with six components for the d functions. The SCF and CASSCF energies are collected in Table 3. The improvement in the energy arises from the correlation of the four π electrons and also from an improved description of the σ electrons. The 'inactive' orbitals in the CASSCF calculation are allowed to relax, in a self-consistent manner, in the field of the correlated π electrons.

A spin-coupled calculation for CH_2N_2 was then carried out for the four π electrons, with the σ-electrons accommodated in the inactive CASSCF natural orbitals. Contour plots for these spin-coupled orbitals are essentially indistinguishable from those in Figures 3 and 4. It appears that allowing the 'core' to relax has a negligible effect on the form of the spin-coupled orbitals. The small difference in energy between the CASSCF and spin-coupled wavefunctions arises from the small contributions from ionic spin-coupled configurations, It should be clear that the spin-coupled wavefunction is very much easier to interpret than the CASSCF wavefunction, which has significant contributions from many of the twenty configurations.

Fulminic Acid.—Calculations analogous to those for CH_2N_2 were carried out for HCNO, which was treated as a planar molecule in the spirit of 1,3-dipoles taking part in cycloaddition reactions as systems with four π electrons. In view of the results for CH_2N_2, we chose to describe all the remaining electrons using doubly occupied SCF MOs. The calculated energies are collected in Table 1—the spin-coupled wavefunction provides an energy improvement over the SCF description of 112 kJ mol^{-1}, whereas spin-coupled ionic configurations contribute only 1.2 kJ mol^{-1}. The spin-coupled orbitals are shown in Figures 5 and 6, and the overlaps between them are listed in Table 2.

Spin-coupled orbital φ_1 is based on a C(2p) function but is distorted towards N, and orbital φ_2 is based on N(2p) but is distorted towards C. The dominant mode of spin coupling with $c_{02} = 0.996$ (99.3% of the wavefunction) corresponds to singlet coupling of the spins associated with these two orbitals. Orbital φ_4 is essentially a slightly deformed O(2p) function and has an overlap of 0.830 with orbital φ_3, which is delocalized over the N and O centres. The descriptions of the π-electron systems in diazomethane and fulminic acid are fairly similar except for the degree of deformation or delocalization of orbital φ_3. Although this orbital in HCNO is so distorted as to have a larger amplitude on oxygen than on nitrogen, the N atom is still taking part in more than four covalent bonds and can be considered hypervalent. The bonding in 'planar' HCNO can be regarded as consisting of a double bond between C and N, and a polar multiple bond (of non-integral order) between N and O.

Nitrone.—It seems likely that nitrones were initially named following a mistaken analogy with ketones. Certainly, the dipole moment of 3.55 D for *N*-methyl-*C*-phenylnitrone is usually taken to indicate the dominance of the azomethine *N*-oxide structure $C{=}N^+{-}O^-$ with appreciable negative charge on oxygen, and only weak diradical character. Nonetheless, a number of theoretical studies have suggested weights in the range 20–45% for the diradical structure,[3,4,16] The spin-coupled calculations presented here for CH_2NHO are essentially the same as those in a previous publication,[18] but a very brief account is included so that we may compare with the other systems.

In this case, the spin-coupled wavefunction provides an energy improvement over the SCF description of 140 kJ mol^{-1} and spin-coupled ionic structures contribute only 1.4 kJ mol^{-1} (see Table 1). The four π orbitals (a'' symmetry in the C_s point group) are shown in Figure 7 and the overlaps between them are

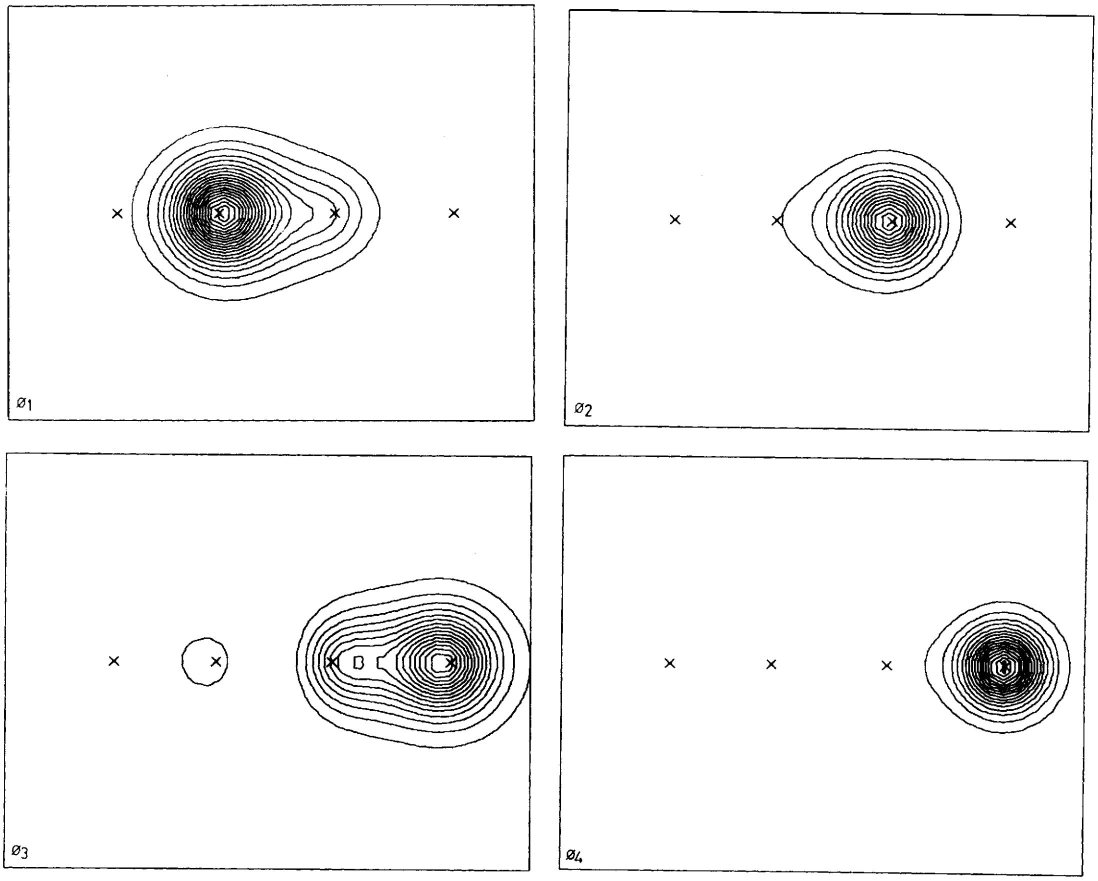


Figure 5. Contour plots for HCNO of $|\varphi_\mu(r)|^2$ in the plane 1 bohr above the 'molecular plane'.

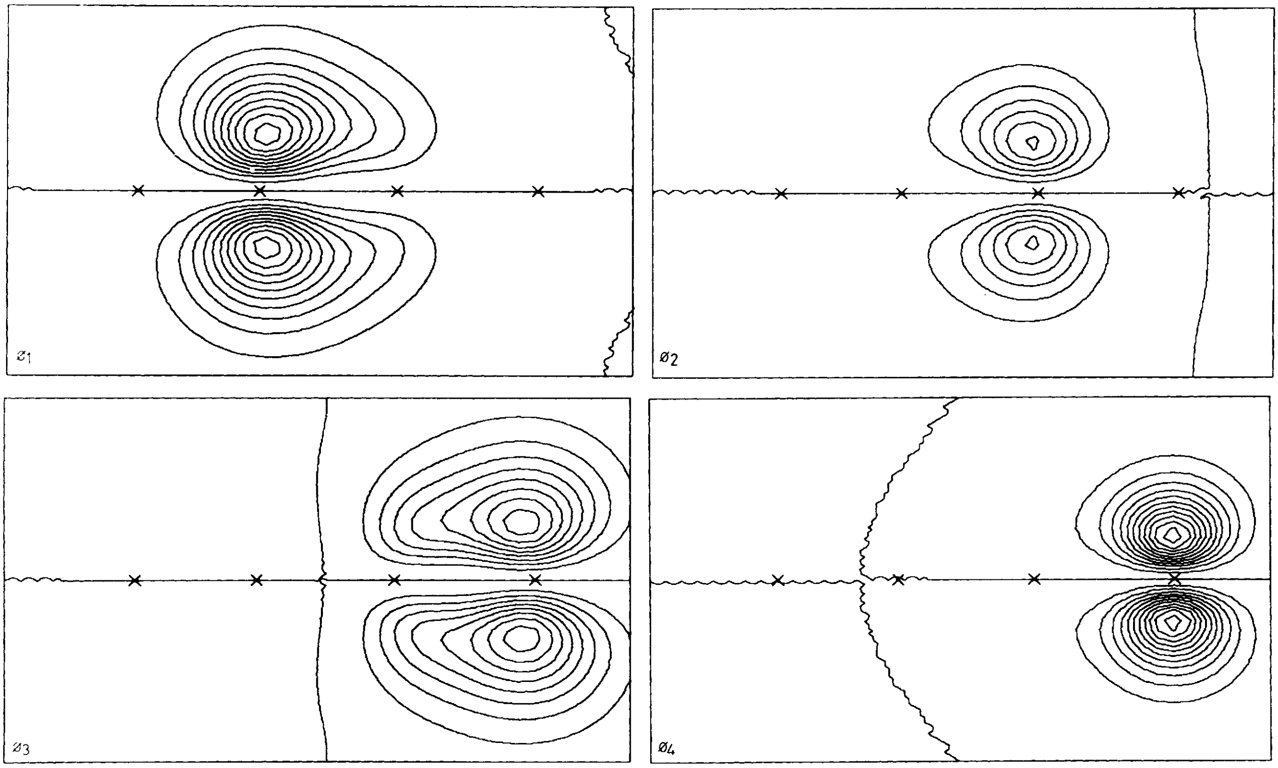


Figure 6. Contour plots for HCNO of $|\varphi_\mu(r)|^2$ in the plane perpendicular to the 'molecular plane' and containing all the atoms.

reported in Table 2. With the orbitals ordered as in Figure 7, the perfect-pairing spin function is again dominant with c_{02} = 0.992 (98.5% of the wavefunction). The bonding in this molecule can be regarded simply as a double bond between C

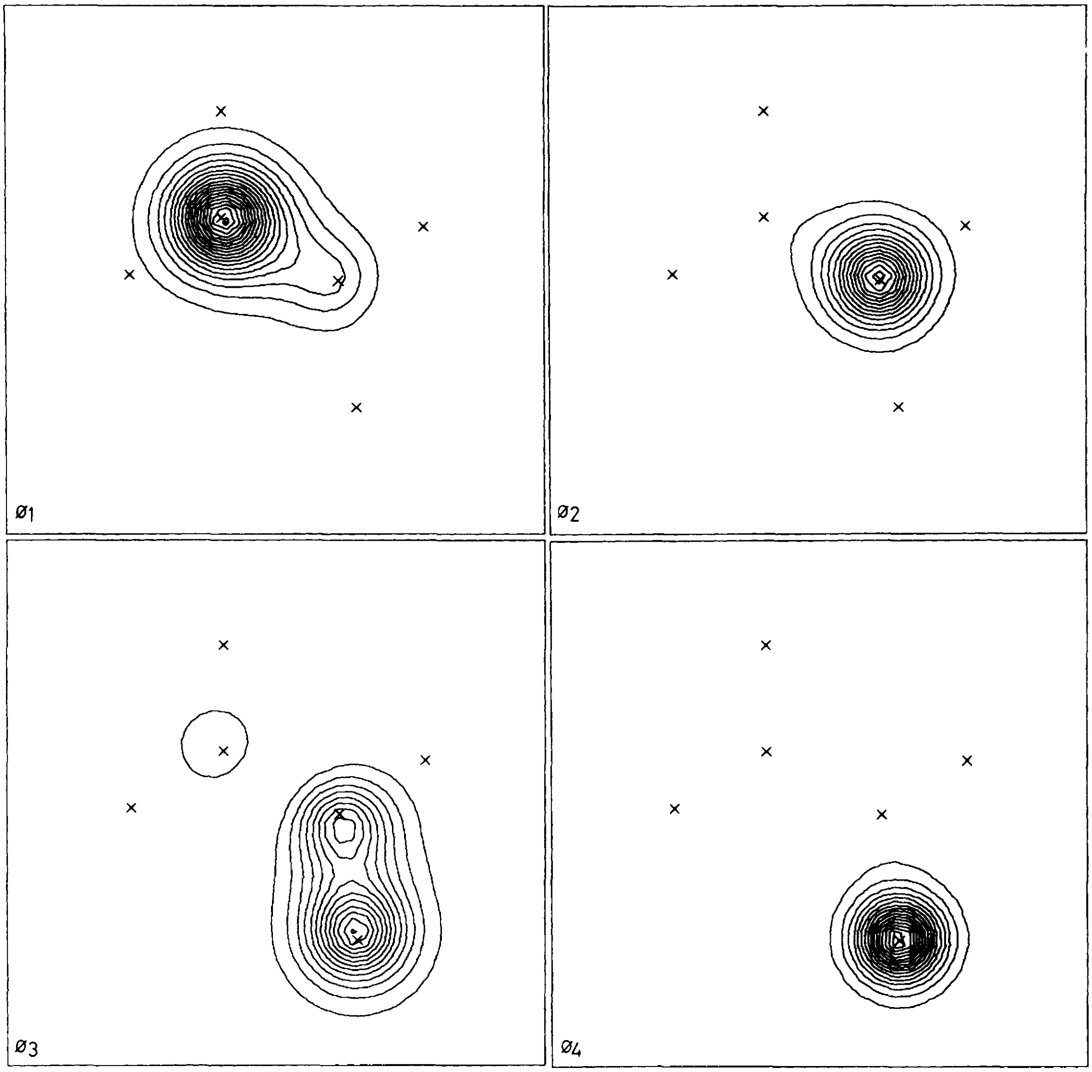
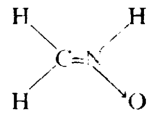


Figure 7. Contour plots for CH_2NHO of $|\varphi_\mu(r)|^2$ in the plane 1 bohr above the molecular plane (σ_h mirror).

and N, and a polar bond between N and O the order of which is *ca.* 1.5. It is perfectly reasonable to represent this molecule with the structure:



An arrow from atom A to atom B signifies that the spin-coupled orbital formally associated with atom A is significantly delocalized onto centre B; this orbital has a large overlap with a spin-coupled orbital that is essentially localized on atom B, and the spins associated with these two orbitals are coupled to a singlet.

It is clear that the spin-coupled descriptions of the four π electrons in nitrone and in 'planar' fulminic acid are very similar. In particular, the change in the CNO angle from HCNO to CH_2NHO seems to have very little effect on the overlap integrals or on the form of the orbitals.

N_2O.—This molecule combines the NN unit as in CH_2N_2 and the NO unit as in HCNO or CH_2NHO, and so it is interesting to see which of these species it resembles most. As before, calculated energies for the 'planar' species are reported in Table 1. The spin-coupled wavefunction affords an energy improvement over that from the SCF calculation of 124 kJ mol^{-1}, with a further lowering of only 1.2 kJ mol^{-1} when spin-coupled ionic structures are included.

Contour plots of the four spin-coupled π orbitals are shown in Figures 8 and 9, and the overlap integrals are recorded in Table 2. Orbital φ_1 is associated with N_A, φ_2 with N_B, φ_4 with O, and φ_3 with both N_B and O. With this ordering of the orbitals, the perfect-pairing spin function is dominant with $c_{02} = 0.992$ (98.5% of the wavefunction). The spin-coupled description for the four π electrons of 'planar' N_2O appears to resemble closely that for CH_2NHO and for 'planar' HCNO.

Ozone.—Calculations were carried out for ozone within the constraint of σ–π separation, as for the other systems discussed so far. The energy improvement from SCF to spin-coupled is very large (262 kJ mol^{-1}), with a further lowering of only 0.8 kJ mol^{-1} on including spin-coupled ionic structures. The resulting spin-coupled π orbitals are shown in Figure 10, and the overlap integrals are listed in Table 2. The two orbitals on the central oxygen atom (φ_2 and φ_3) have a large overlap (0.817) but the corresponding spins are not coupled to a singlet. Instead, the perfect-pairing spin function is dominant with $c_{02} = 0.999$ (99.8% of the wavefunction) and this corresponds to two O–O π

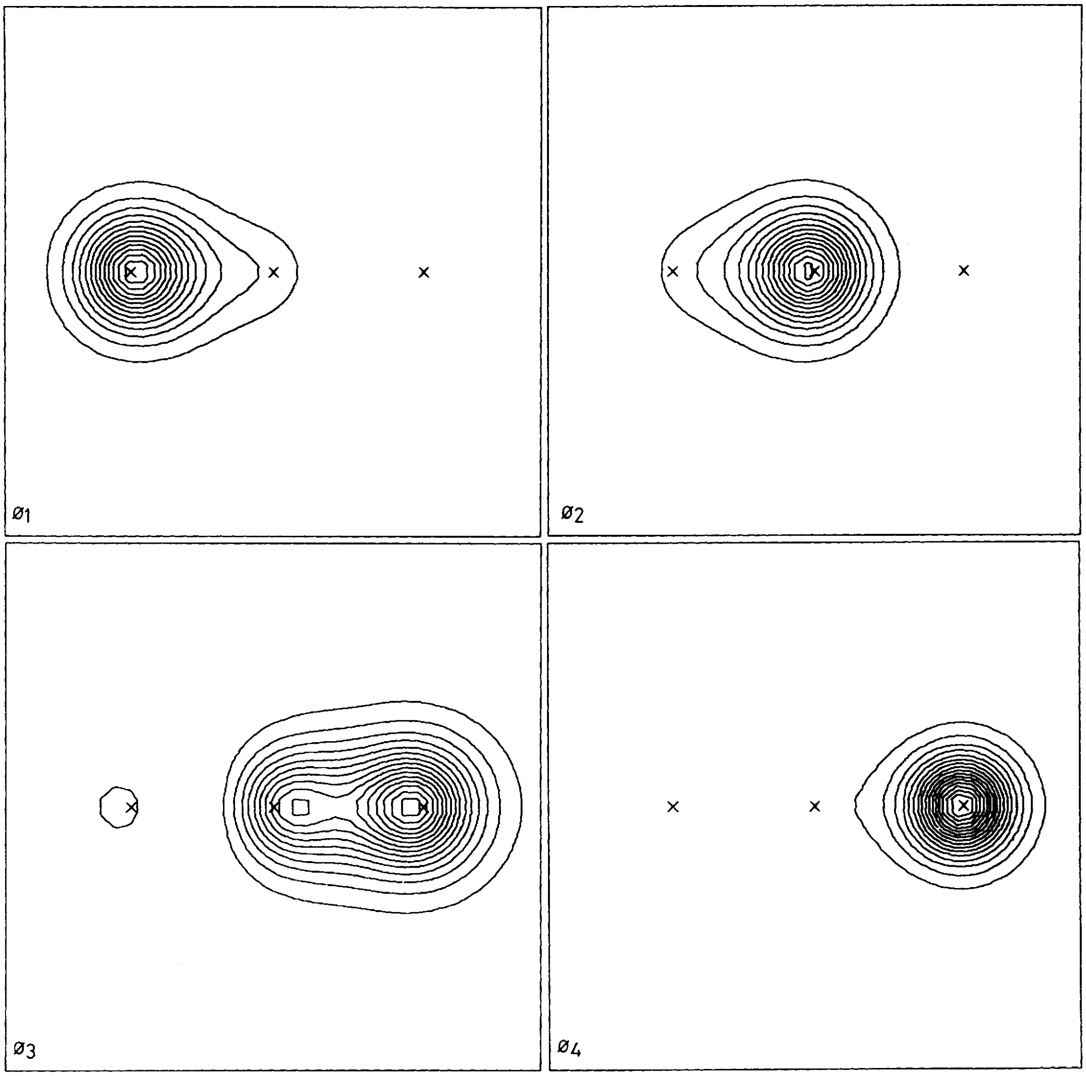


Figure 8. Contour plots for N_2O of $|\varphi_\mu(r)|^2$ in the plane 1 bohr above the 'molecular plane'.

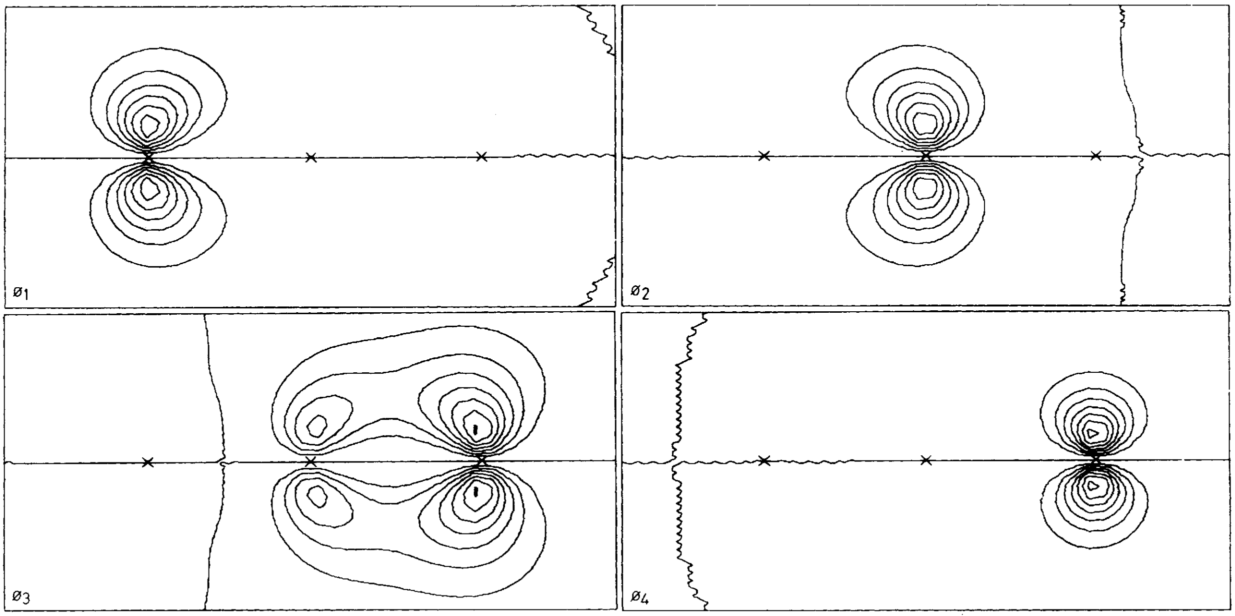


Figure 9. Contour plots for N_2O of $|\varphi_\mu(r)|^2$ in the plane perpendicular to the 'molecular plane' and containing all the atoms.

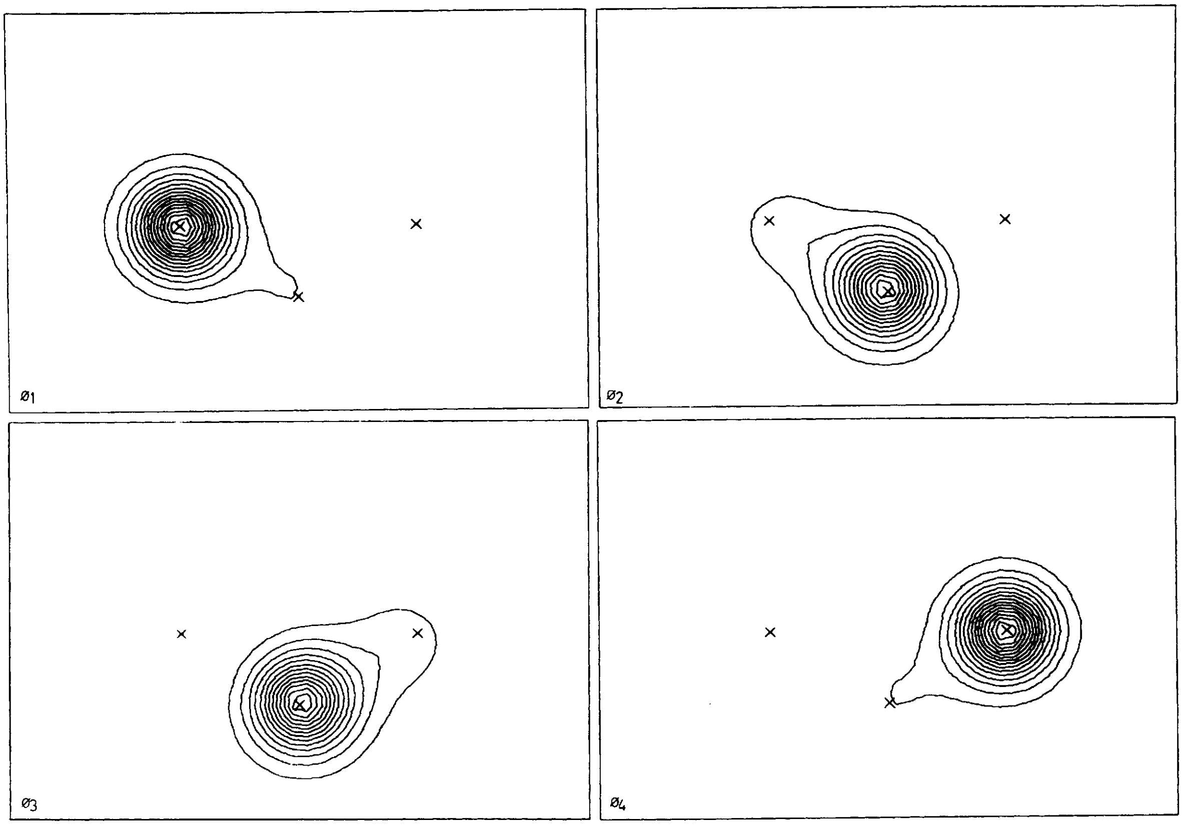
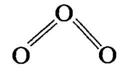


Figure 10. Contour plots for O_3 of $|\varphi_\mu(r)|^2$ in the plane 1 bohr above the molecular plane (σ_v' mirror).

bonds, with negligible diradical character. We may thus represent the molecule by the structure:



with a hypervalent central atom, where the lines drawn between the atoms have the same significance as for diazomethane. We return later to the question of 'lone-pairs' in all of these molecules.

NO_2.—Although the five spin-coupled orbitals for NO_2 were optimized without any constraints on their symmetry or on the overlaps between them, we find that φ_1–φ_4 have pure π symmetry (*i.e.* they are antisymmetric with respect to reflection in the molecular plane) and φ_5 has pure σ symmetry. The overlaps between the orbitals are listed in Table 2, and the π orbitals are shown as contour plots in Figure 11. In this case, the energy improvement over the SCF description is 137 kJ mol^{-1} (see Table 1). The further lowering on including spin-coupled ionic configurations for the π electrons (25 VB structures in all) is less than 0.3 kJ mol^{-1}.

Orbital φ_1 is fairly localized on O_A, but φ_2 is delocalized over both N and O_A. φ_4 and φ_3 are the corresponding orbitals in the NO_B bond. The dominant mode of spin coupling has $c_{\frac{1}{2}5}$ = 0.999 (99.9% of the wavefunction) and this corresponds to perfect pairing of the spins of the π electrons. It appears that our description of the bonding in NO_2 is fairly similar to that for the analogous bonds in CH_2NHO and in 'planar' N_2O and HCNO.

Discussion

The picture that emerges for the π-electron systems on the three heavy atoms, ABC, of these planar 1,3-dipoles is remarkably simple. It is useful to consider the bonding in terms of two π orbitals (φ_2 and φ_3) on atom B, and one on each of A and C (φ_1 and φ_4, respectively). In spite of the fact that the two orbitals on the central atom have a very large overlap, the corresponding electron spins do not pair up to form a net singlet spin, as we might have expected. Such a situation would correspond to a diradical structure. Instead, the dominant mode of spin coupling is that in which electrons 1 and 2 are coupled to a singlet, and similarly the spins of electrons 3 and 4: the spins associated with the orbitals on B are coupled with those of their neighbours on atoms A and C.

The distortion of all the orbitals away from pure atomic functions is consistent with the dominance of the perfect-pairing mode of spin coupling. In particular, φ_2 distorts towards A and φ_3 distorts towards C. In diazomethane and ozone, for example, we can recognize two fairly ordinary π bonds, so that the central atom is hypervalent. This remarkable phenomenon is the result of subtle electron correlation effects. The further distortion effects in some of the systems appear to reflect the differences in electronegativity. When A and C are different, and C is more electronegative than B, then orbital φ_3 may be so distorted towards C that it becomes a two-centre orbital, and may even have its maximum amplitude on atom C. This is the situation when the heavy-atom backbone is NNO or CNO.

The hypervalent character of the central heavy atom in these molecules has emerged naturally without any preconceptions on our part as to the nature of the bonding in the π-electron system. The form of the orbitals and the dominance of a particular mode of spin coupling provides a straightforward rationalization of the short bond lengths observed experimentally. This surprising, but very simple description is a consequence of the inclusion of electron correlation effects into the model from the outset.

It is important to examine also the consequences of our

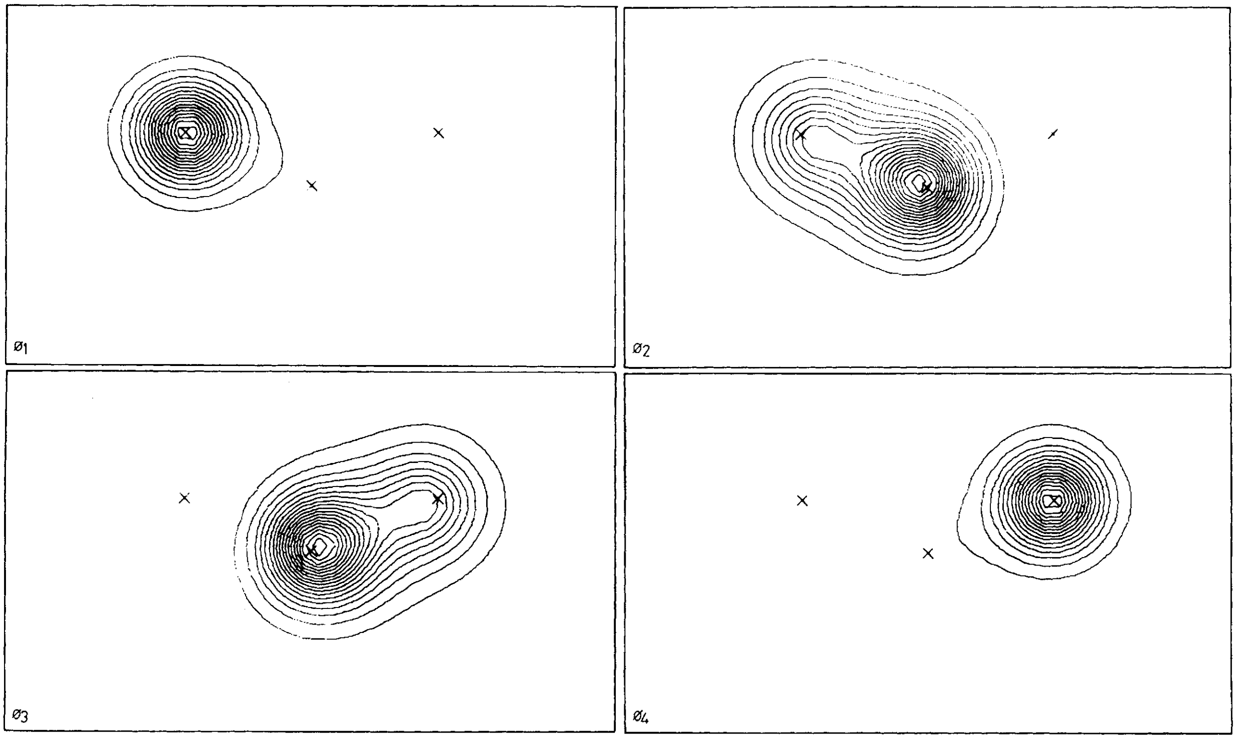


Figure 11. Contour plots for NO_2 of $|\varphi_\mu(r)|^2$ in the plane 1 bohr above the molecular plane (σ_v' mirror).

picture for the chemistry of the 1,3-dipoles, and a detailed study is in progress to model 1,3-dipolar cycloaddition reactions. The aim is to understand, in terms of our language, the principles which govern reactivity and regioselectivity. Results will be published in due course. A puzzling feature is the apparent success, in some cases, of frontier orbital arguments based on wavefunctions which do not represent well the electronic structure of these molecules.

In our model of the bonding in the π-electron system, the central nitrogen atom N_A of diazomethane is utilizing all of its valence electrons in bonding. This appears to be consistent with the high resilience of this atom to attack by nucleophiles or electrophiles, especially when compared with its neighbours or to nitrogen atoms in other π-electron systems. It is a general feature of 1,3-dipoles that the formation of a new bond to the hypervalent centre is very difficult.

The only reaction which the central N atom of CH_2N_2 will undergo readily is cleavage of the bond to the carbon atom, so as to produce a carbene and N_2. The explosive nature of this last reaction raises a number of interesting questions, such as whether this tendency of diazo compounds might be linked in some way to the hypervalent nature of the bonding. Some support for this idea comes from the nature of other explosives such as ozone, which also features a hypervalent atom. Following our discussion of the NO_2 radical, it seems likely that nitro compounds, one of the mainstays of the explosives industry, are also based on hypervalent nitrogen atoms. Presumably azides, and many other shock-sensitive and explosive materials, fit into this category also. Modelling the detonation characteristics of such explosives is a complex task. Work is in hand to examine the effects on the form of the orbitals and on the mode of the spin coupling in CH_2N_2 of shortening and lengthening bond lengths, in order to simulate one aspect of the consequences of a shock. For nitro compounds, it will be especially useful to assess the influence of the rest of the molecule on the bonding in the $-NO_2$ group, and also the effects of bringing up other functional groups such as $-CH_3$ or $-NH_2$.

It seems very unlikely that our mechanism for the bonding in 1,3-dipoles is restricted to this particular class of molecules. Consider, for example, the linear molecule XeF_2. It is easy to envisage that six of the valence electrons on xenon occupy approximately sp^2 hybrid orbitals, pointing perpendicular to the molecular axis, and that the two remaining electrons are accommodated in $5p_z$ orbitals. In this model, these last two orbitals would polarize towards different fluorine atoms, each of which has a single electron in a $2p_z$ orbital. Depending on the degree of polarization of the two orbitals on xenon, each of the $F(2p_z)$ orbitals may have a very considerable overlap with the xenon orbital pointing towards it. Provided that the spins associated with these xenon orbitals are not coupled with each other, but are instead singlet coupled with the spins of electrons on the fluorine atoms, then we would obtain two fairly normal Xe–F bonds. Although this description of the bonding in XeF_2, and of other noble gas compounds, is very plausible, detailed calculations are now required to confirm its validity. There might also be a role for hypervalent atoms in attempts to understand the magnetic properties of transition metal oxides and the mechanism of 'high'-T_c superconductivity.

This work has concentrated on the four π electrons of planar 1,3-dipoles, as have most previous theoretical discussions. For the NO_2 radical, the calculations were carried out for five 'active' electrons without symmetry constraints, but it turns out that four of the spin-coupled orbitals for this system have pure π symmetry and that the unpaired electron occupies an orbital of pure σ symmetry. In the case of the second set of calculations on CH_2N_2, the doubly occupied σ orbitals were allowed to relax, in a self-consistent manner, in the field of the correlated π electrons. This improved description of the σ 'core' did not alter our physical picture of the bonding in the π-electron system. Further refinements, such as the use of, say, a perfect-pairing GVB description for the σ electrons, are unlikely to have any significant effect on our model, and similar conclusions can be expected for the other molecules considered in this work.

In order to carry out a more sophisticated treatment of these molecules, we need to treat all of the bonding and non-bonding σ electrons on an equal footing with the π electrons. It is important to discover whether the σ–π separation arises naturally in a fully non-orthogonal variational treatment, or whether the different symmetries mix to some extent in some of these systems. Only when such calculations have been completed will it be possible to provide a definitive description of the 'lone-pairs' in molecules such as ozone.

The σ–π separation invoked in our calculations on these 1,3-dipoles is an approximation which can be justified to a large extent by considering the cycloaddition chemistry of these molecules. It seems likely that more detailed calculations, with much larger numbers of 'active' electrons, will confirm the main features of our rather unexpected, albeit very simple picture of the bonding in these π-electron systems. The results of such calculations, as well as studies of cycloaddition reactions and of detonation processes, will be reported in due course.

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