The Extraordinary Electronic Structure of N_2S_2

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Abstract: The electronic structure and bonding of the N_2S_2 molecule are studied by the spin-coupled valence bond method. Unusual features are revealed which clarify much of the hitherto puzzling properties of this molecule, leading ultimately to a simple Lewis structure: The two N atoms of the N_2S_2 ring bear a substantial negative charge, and the two S atoms, a complementary positive charge. There are four single N−S σ bonds and two lone pairs of π electrons, one pair centered about each N atom. Two further π electrons, one from each of the S atoms, are directly coupled to each other across the ring, giving the molecule the overall character of a singlet diradical. This last is shown to be closely related to the metallic character of the $(SN)_x$ polymer.

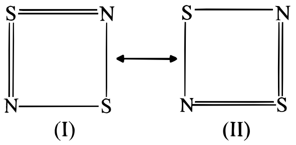
1. Introduction

According to Greenwood and Earnshaw,[1] the geometry of the N_2S_2 molecule is almost exactly a square, in spite of the disparity in the sizes of the S and N atoms: The S−N bond lengths, determined from X-ray diffraction studies, are 165.1 and 165.7 pm, and the S−N−S bond angle is 90.4°, while the N−S−N angle is 89.9°. At room temperature, N_2S_2 readily polymerizes to form $(SN)_x$, which is metallic. At very low temperatures (0.33 K), the polymer becomes superconducting. There is consequently much about this system to warrant a close study of the N_2S_2 monomer itself.

The nature of the bonding in N_2S_2 is far from obvious. A favorite first-year university examination question is "N_2S_2 is said to be aromatic. Discuss." The answer is meant to be that the molecule is planar and possesses six electrons in orbitals of π symmetry, which implies some similarity to the benzene molecule. The purpose of this paper is to show that nothing could be further from the truth.

We do this using the spin-coupled valence bond (VB) method. The spin-coupled wave function incorporates much chemically significant electron correlation in a compact and highly visual form. This approach to the determination of molecular electronic structure is described in detail in several places (see, *e.g.*, ref 2) and is outlined in the following section.

A great deal of work has been carried out on various aspects of the electronic structure of N_2S_2, particularly its gas phase UV−photoelectron spectrum (see, *e.g.*, refs 3−18). In particular, Findlay *et al.*[11] carried out an SCF calculation and attempted to correlate the calculated orbital energies with the observed photoelectron spectrum. In addition, they localized the MOs by means of the method of Foster and Boys[20] and obtained a structure which is symmetry-broken, but without any cross-ring bonding (**I**). This has led to a description of the bonding in N_2S_2 as a resonance primarily between structures such as **I** and **II**, and which is reproduced in ref 1. This, rather than any supposed aromaticity of N_2S_2, appears to be the currently accepted view of the electronic structure of this molecule. However, this picture provides no explanation of the unusual properties of N_2S_2. Harcourt and Skrezenek, in contrast, consider N_2S_2 to be a spin-paired diradical with a long N−N bond across the ring.[17,18]



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But in an earlier paper, Adkins and Turner[3] had localized the MOs in their CNDO/2 wave function for N_2S_2 by using the method of Edmiston and Ruedenberg.[19] In contrast to Findlay *et al.*, they found a single symmetry-adapted configuration, consisting of two three-centered LMOs of π symmetry, centered about the N atoms and an S−S nonbonding π orbital of the form $S_1(3p\pi)-S_2(3p\pi)$. The total charges on the atoms were found to be +0.21 for the S atoms and complementary negative charges for the N atoms. We return to their results below. In the largest MO−CI investigation to date, Palmer and Guest[14] determined a number of singlet and triplet excited states of N_2S_2 and gave a detailed discussion of the role of certain excited states in the mechanism of polymerization of N_2S_2.

2. Calculational Method

The spin-coupled wave function Ψ_{SM} is written as

$$\Psi_{SM} = \mathcal{A}\{\psi_1^2\psi_2^2...\psi_{n_c}^2\phi_1\phi_2...\phi_N\Theta_{0,0}^{2n_c}\Theta_{S,M}^N\} \qquad (1)$$

Here there are N spin-coupled or active orbitals ϕ_μ (μ = 1, 2, ..., N) and n_c doubly-occupied orbitals ψ_i (i = 1, 2, ..., n_c) which form an inactive core. The spin-coupled orbitals are distinct, singly-occupied, and *nonorthogonal*. Both core and valence orbitals are expanded in a set of m basis functions χ_p (p = 1, 2, ..., m):

$$\psi_i = \sum_{p=1}^{m} c_{ip}\chi_p; \quad \phi_\mu = \sum_{p=1}^{m} c_{\mu p}\chi_p$$

The spin function $\Theta_{0,0}^{2n_c}$ in eq 1 is the appropriate function for the inactive electrons:

$$\Theta_{0,0}^{2n_c} = \sqrt{\frac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\sqrt{\frac{1}{2}}(\alpha_3\beta_4 - \beta_3\alpha_4) \; ...$$

By contrast, $\Theta_{S,M}^N$ is the N-electron spin function for the active electrons. It is formed as a linear combination of individual spin functions $\Theta_{S,M;k}^N$, in which the index k denotes a particular coupling or pairing scheme,

$$\Theta_{S,M}^N = \sum_{k=1}^{f_S^N} c_{Sk}\Theta_{S,M;k}^N \qquad (2)$$

and the sum runs over all f_S^N allowed modes of coupling. All orbital coefficients, c_{ip}, $c_{\mu p}$, and the spin-coupling coefficients c_{Sk} are optimized simultaneously, without any preconceptions as to the ultimate forms of the orbitals, or to the type of coupling between the electron spins (see, *e.g.*, ref 25). Frequently the spin-coupled orbitals are highly localized and have the familiar shape of hybridized atomic orbitals, albeit in a somewhat distorted form. The total energy afforded by the spin-coupled wave function is usually within a few millihartrees of that given by a "complete active space" SCF function (CASSCF) for N electrons in N orbitals.

In one noteworthy application, the spin-coupled VB method was used to demonstrate a picture of the π electrons of benzene which is quite different from the well-known molecular orbital view,[24] while yielding 92% of the full valence correlation energy, *i.e.*, yielding 92% of the difference between the energy of the SCF wave function and that of a full CI wave function for six active electrons distributed among six π orbitals (the three occupied plus three unoccupied π MOs of lowest energy). In general the spin-coupled energy yields 85−95% of the full valence correlation energy in a given basis.

Table 1. Calculated Total Energies[a]

calculation, DZP basis set	total energy
Hartree−Fock	−903.784 34
SC: 6 π electrons (optimized core)	−903.847 522
SC: 8 σ electrons (optimized core)	−903.855 273
SC: 14 electrons (frozen core)	−903.912 341

[a] In au.

A standard closed-shell SCF calculation on N_2S_2 was carried out using the GAMESS(UK) code.[21] An idealized nuclear geometry, very close to experiment, was used consisting of a square of side 165.4 pm, thus assuming an overall symmetry of D_{2h} for the molecule. A standard Dunning double-ζ (DZ) basis set,[22] consisting of 56 basis functions, was employed, followed later by calculations with a double-ζ-plus-polarization (DZP) basis (80 basis functions, including d orbitals on both N and S), in order to confirm our results.

Calculations were also carried out at a nuclear geometry obtained by optimization of the SCF wave function. However, the subsequent spin-coupled calculations gave a much higher total energy than that obtained at the idealized nuclear geometry above. Otherwise the wave functions obtained, SCF and spin-coupled, were very similar.

Examination of the DZ SCF output provides the first hint of something unusual: The Mulliken populations of the N atoms are ~7.8 while those of the S atoms are ~15.2, indicating that the N atoms are almost completely negatively charged and, correspondingly, the S atoms are almost completely positive. We found it impossible to localize the occupied π orbitals, either by using the Foster and Boys technique,[20] by the population localization criterion,[23] or by the Edmiston−Ruedenberg method.[19] These results remain essentially unchanged on using even larger bases, such as triple-ζ-valence plus polarization (TZVP) basis sets.

Spin-coupled calculations were carried out on N_2S_2 in the DZ basis, treating six electrons as active. The total energies obtained are shown in Table 1, and the resulting spin-coupled orbitals are plotted in Figure 1. The six orbitals turn out to be of π symmetry, although no such constraints were imposed upon the calculations. The contours are plotted in a plane parallel to that of the molecule and 1 bohr above it. The corresponding overlap integrals $\langle\phi_\mu|\phi_\nu\rangle$ between the orbitals are shown in Table 2.

From Figure 1, we see immediately that on each of the two S atoms there is indeed only a single π orbital: orbitals ϕ_1 and ϕ_2, respectively. It can be seen that they are well localized. Each N atom also has a single highly localized π orbital centered upon it (orbitals ϕ_4 and ϕ_5, respectively). In addition to this, there are two three-center π orbitals, symmetrically related to each other, centered about each N atom and stretching over the two S−N−S subsystems (orbitals ϕ_3 and ϕ_6). The sulfur atoms bear a significant positive charge, +0.52*e* in the DZP basis, and the nitrogen atoms a complementary negative charge.

A transposition of orbitals ϕ_1 and ϕ_2, the π orbitals on the S atoms, is equivalent to a symmetry operation of the molecule: *i.e.*, the transposition is equivalent to a reflection in a plane perpendicular to that of the molecule and passing through both N atoms. Since the total electronic wave function for the ground state, Ψ_{00}, belongs to the totally symmetric representation A_g of D_{2h}, it must remain invariant under this operation. Consequently Ψ_{00} must be symmetric toward interchange of the spatial coordinates of the two electrons described by ϕ_1 and ϕ_2. This means that, in a state of symmetry A_g in D_{2h}, the spins of the

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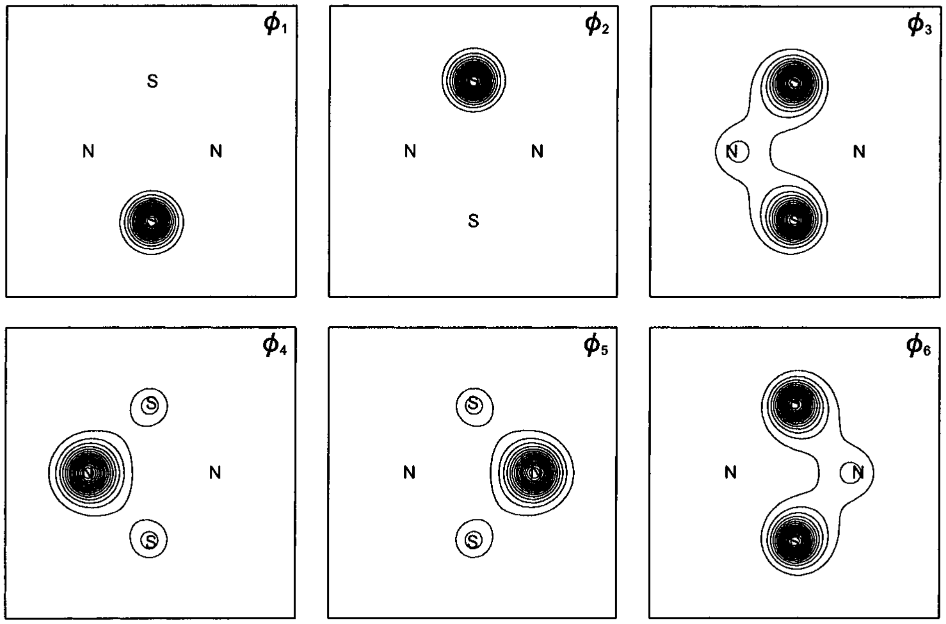

Figure 1. N_2S_2 orbitals of π symmetry. The contours are of $|\phi_\mu|^2$ drawn in a plane parallel to the molecular plane and 1 bohr above it. Orbital ϕ_2 is obtained from ϕ_1 by a reflection in a plane perpendicular to the S−S axis and passing through both N atoms. Orbital ϕ_6 is obtained from ϕ_3 and ϕ_5 from ϕ_4 by a reflection in a plane perpendicular to the N−N axis and passing through both S atoms.

Table 2. Overlap Integrals between the Spin-Coupled Orbitals for 6 π Electrons: DZP Basis

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1	1.000	−0.595	0.339	0.124	0.124	0.339
ϕ_2		1.000	0.339	0.124	0.124	0.348
ϕ_3			1.000	0.766	0.480	0.825
ϕ_4				1.000	0.327	0.480
ϕ_5					1.000	0.766
ϕ_6						1.000

Table 3. Spin-Coupling Coefficients, Kotani Basis

$\Theta_{S,M;k}$	6 π electrons; DZP basis	$\Theta_{S,M;k}$	6 π electrons; DZP basis
1	0.0	4	−0.182 554
2	0.0	5	0.983 196
3	0.0		

Table 4. Calculated Mulliken Populations

active electrons, DZP basis set	Mulliken population	
	N	S
Hartree−Fock	7.56	15.44
6 SC π electrons	7.52	15.48
8 SC σ electrons	7.55	15.46
14 SC electrons (8 σ, 6 π)	7.26	15.74

electrons in ϕ_1 and ϕ_2 must be coupled exactly to a singlet. Of the five possible spin functions for six electrons and net spin $S = 0$, we find that the only nonzero spin-coupling coefficients are indeed the two corresponding to spin functions where electrons 1 and 2 are coupled to a zero spin (see Table 3). The preponderance of the "perfectly paired" spin function (spin function 5 in Table 3), whose coefficient is 0.983, should be noted, *i.e.*, the spins of orbital pairs (ϕ_1,ϕ_2), (ϕ_3,ϕ_4), and (ϕ_5,ϕ_6) are to an excellent approximation simply paired up in singlets.

3. Discussion

From an initial glance at these results, one might conclude that there is a direct S−S π bond. However, further examination of orbitals ϕ_1 and ϕ_2 (*i.e.*, in a plane perpendicular to the molecular plane and passing through both S atoms) shows that this is not so, as can be seen in Figure 2.

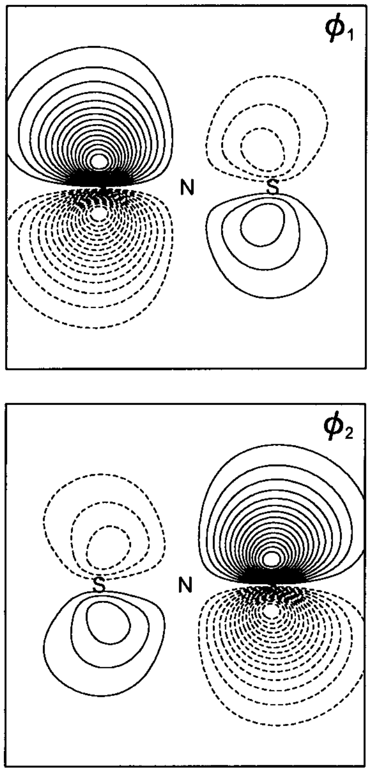

Figure 2. Contours of orbitals ϕ_1 and ϕ_2 drawn in a plane perpendicular to the molecular plane and passing through both S atoms. The positions of the two S atoms are indicated as well as those of the two N atoms. Note that the N atoms lie in planes above and below that of the two sulfur atoms.

Orbitals ϕ_1 and ϕ_2 each possess a nodal surface, roughly halfway between the two S atoms; the lobes of ϕ_1 and ϕ_2 are bent slightly away from the other S-atom partner, and the total electron density actually decreases within the N_2S_2 ring. These nodal surfaces originate from the radial nodal surfaces present in the 3p orbitals of sulfur.

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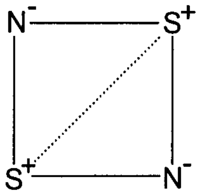

Figure 3. Schematic drawing of the bonding in N_2S_2.

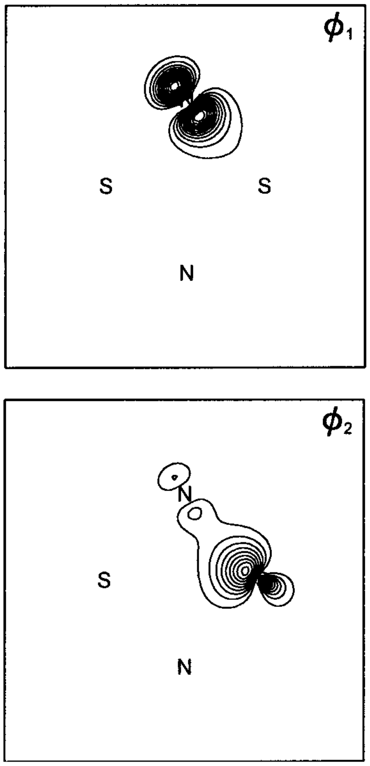

Figure 4. Two of the orbitals which form an N−S σ bond. By symmetry the other three N−S σ bonds are similar. The contours are of $|\phi_\mu|^2$ drawn in the molecular plane.

This conclusion is further borne out by the pattern of critical points found in a topological analysis (Bader analysis) of the spin-coupled wave function.[26,27] The absence of a (3,−1) critical point in the center of the molecule clearly indicates the absence of any diagonal (*i.e.*, S−S or N−N) bonds.

Normally when two orbitals on different atoms overlap and the spins of the electrons occupying each of them are paired up, we consider this to be a single bond. Otherwise if the two orbitals happen to be orthogonal, either exactly by symmetry or effectively so due to the distance between them, the lowest state is usually obtained when the electron spins are coupled to a triplet. The molecule is then referred to as a diradical. In N_2S_2, a different situation arises: Orbitals ϕ_1 and ϕ_2 overlap, and the corresponding spins are coupled to a singlet. Yet no true bond is formed. We therefore consider that N_2S_2 in its ground electronic state is best described as a *singlet diradical.*

The two diffuse π orbitals ϕ_3 and ϕ_6 deserve comment. To a certain extent, we have observed similar behavior on several previous occasions: Two orbitals which might be thought of as a "lone pair" (such as ϕ_3 and ϕ_4 here) often have the form where one of the orbitals is tightly bound to a particular atom, while the second is much more diffuse. This disparity introduces as much "radial" correlation as possible between the two electrons occupying these orbitals. In the present case, the diffuse orbitals actually extend over three centers S−N−S, and whether they can be considered as highly deformed π(N) orbitals is a moot point. The overlap between the pairs ϕ_3 and ϕ_4, and between ϕ_5 and ϕ_6, is 0.766 in the DZP basis, and the net spin of each of these pairs of orbitals is almost exactly a singlet.

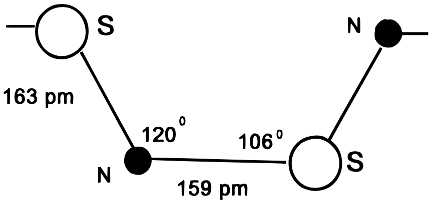

Figure 5. The structure of the $(SN)_x$ polymer.

However, one should note (see Table 3) that the overlap between the two most diffuse orbitals, ϕ_3 and ϕ_6, is as much as 0.825 in the DZP basis. The extent of this delocalization serves to even out, to some degree, the charge differences between neighboring atoms. Nevertheless, the spin-coupling coefficients clearly indicate that, in spite of their large overlap, the spins of these two electrons are not paired with each other. In fact the overwhelming predominance of the singlet pairing between the lone pair orbitals (ϕ_3,ϕ_4) and (ϕ_5,ϕ_6), which is by no means a necessary outcome of the calculation, is a good indication, in spite of the considerable delocalization of ϕ_3 and ϕ_6, of the absence of any specific interaction between them and the S(π) orbitals which constitute the singlet diradical aspect of the molecule. The small value of the overlap between ϕ_3 or ϕ_6 with either of the S(π) orbitals, $\langle\phi_1|\phi_3\rangle = \langle\phi_1|\phi_6\rangle = 0.339$, further emphasizes this last point.

A moment's thought will convince one that this bonding pattern is in accord with all the valencies within this single "spin-coupled structure", though in a highly unexpected manner: N^- ions have a valency of 2 and accordingly form two single bonds of σ symmetry with a bond angle between them of 90°, one with each of the neighboring S atoms. The S^+ ions have a valency of 3, and accordingly they each form two bonds of σ symmetry with adjacent N^- ions. We thus have a σ single bond framework for N_2S_2. The remaining two electrons each occupy a single π orbital on each S atom and are singlet coupled to each other. Because the orbitals involved are purely π in character, the question of bond angles does not arise. N_2S_2 can therefore be represented reasonably well by the bonding scheme shown in Figure 3 in which the dotted line joining the two S atoms indicates the singlet diradical character of the link.

However, since only the six electrons described by orbitals of π symmetry have been taken into account, it remains to confirm this picture. In particular, one should also consider the eight electrons which form the σ bonds, *i.e.*, one should take into account at least 14 active electrons.

In order to achieve this, further calculations were carried out in which eight orbitals of σ symmetry are alone regarded as active. Two of these orbitals which form one of the N−S σ bonds are shown in Figure 4.

The figure clearly shows a single σ bond, constructed from the overlap between a somewhat deformed 2pσ function, stemming from nitrogen, pointing directly toward a neighboring S atom, and a deformed 3pσ orbital on S, pointing directly at N. Because of the difference in electronegativity between the N and S atoms, the deformation of the S(3pσ) orbital is considerably more pronounced than that of the N(2pσ) orbital: Figure 4 shows that the S(3pσ) orbital includes considerable N(2pσ) character, thus imparting to the N−S σ-bonded link a distinct $S^{\delta+}N^{\delta-}$ polar character. It should again be emphasized that this is a direct outcome of the calculation: No localization procedures of any kind were carried out or imposed.

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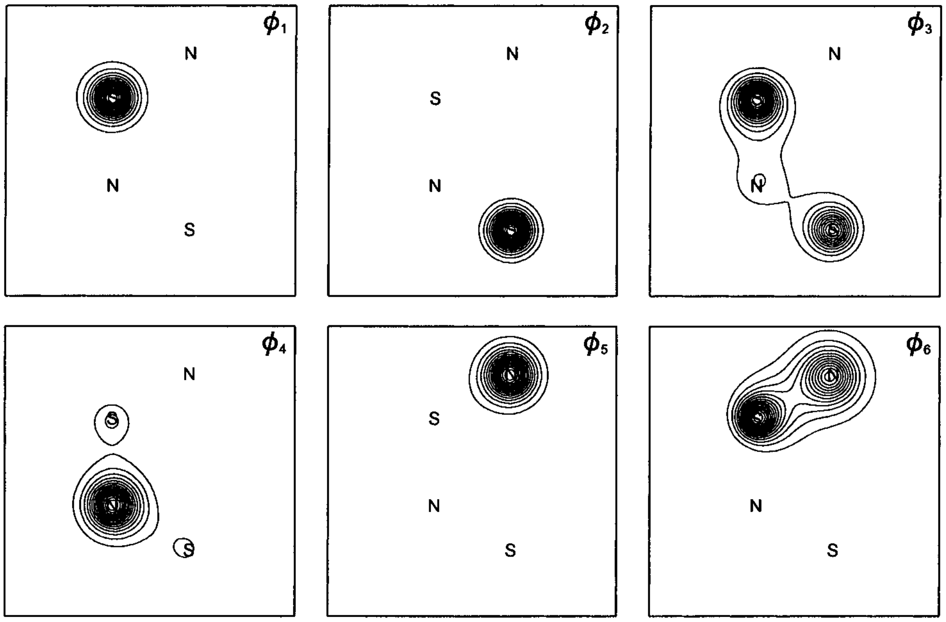

Figure 6. The orbitals of $(SN)_2$ corresponding to the $(SN)_x$ chain.

Finally the sets of six π orbitals and eight σ orbitals were used as a starting guess for a 14-electron calculation.[28] Only a single spin function, that corresponding to perfect pairing, was included. The remaining doubly-occupied orbitals were not optimized, but remained frozen in their Hartree−Fock (SCF) form. The calculation converged in a few iterations, and the resulting spin-coupled orbitals are practically indistinguishable from those already shown. The result of this calculation thus confirms our results obtained using just six electrons in six spin-coupled orbitals of π symmetry. In addition it indicates the absence of any specific σ/π interaction among the valence electrons. It also demonstrates, incidentally, the utility of carrying out separate calculations on smaller parts of a system in order to obtain a good initial guess for the whole.

At this point it is worth recalling the CNDO/2 results of Adkins and Turner,[3] which, it turns out, are remarkably similar to ours. The main difference is in the description of the two π electrons associated with the S atoms which, according to them, occupy a single nonbonding MO which is also the HOMO.

Single-configuration MO theory is not capable of describing a singlet diradical, and in retrospect, a nonbonding MO of the form $S_1(3p\pi)-S_2(3p\pi)$ is the closest approximation possible to this situation.

The most striking feature of the bonding in N_2S_2 is the fact that the electrons in each of the π orbitals of the S atoms do not form a bond with each other, as each of the orbitals involved possesses a nodal surface in a plane perpendicular to the line joining the two S atoms. However, because of the lengths of the N−S bonds, the distance between the S atoms is only 165.6 pm, whereas in almost all N_xS_y compounds, the S−S distances are much longer: ~206−242 pm. Hence for stereochemical reasons, the two S atoms in N_2S_2 are unusually close and there appears to be a fairly strong repulsive interaction between them, reminiscent of a triplet state rather than a singlet.

In order to pursue the apparent similarity of the ground state to a low-lying triplet state, spin-coupled calculations were carried out on what is presumably the lowest triplet state of N_2S_2 at the same geometry as the ground state. The energy of this state was found to lie 2.0 eV above the ground state, and careful analysis of the spin-coupled wave function shows it to possess $^3B_{3u}$ symmetry. In addition, the spin-coupled orbitals associated with the S atoms in this state have a nodal plane passing through both N atoms. This suggests repulsion between the S atoms, so that at the equilibrium nuclear geometry, the S−S separation would be increased relative to that of the ground state. This means of course that, at the minimum, the energy of the $^3B_{3u}$ state is likely to be even closer to the ground state than 2.0 eV. In an earlier *ab initio* SCF calculation, Palmer and Findlay[15] found a 6π-valence triplet state lying at 0.23 eV above the ground state, but in a later MO−CI work, Palmer and Guest[14] report only a $(\pi\pi^*)1^3B_{3u}$ state with a vertical excitation energy of 3.06 eV.

4. The $(SN)_x$ Polymer

Since the N_2S_2 molecule polymerizes with such readiness (itself an indicator of the radical character of the monomer), it is also worthwhile to consider briefly the electronic structure of the polymer in light of these results.

The geometric structure of the $(SN)_x$ chain, which is not completely flat, is shown in Figure 5. We have carried out calculations on N_2S_2 in which two adjacent angles, $S\hat{N}S$ and $N\hat{S}N$, are opened out to 120° and 106°, thus effectively breaking an N−S bond. The resulting π orbitals are shown in Figure 6. It can be seen that a singly-occupied π orbital on each S atom, ϕ_1 and ϕ_2, remains. In addition, the two orbitals forming the lone pair centered on the S−N−S group, ϕ_3 and ϕ_4, in which ϕ_4 is tightly bound around the N atom and the other, ϕ_3, is three-centered, also survive. However, the lone pair associated with what is now the terminal N atom is different: The orbital, ϕ_6, which in N_2S_2 is three-centered, is now only two-centered.

We thus see that the $(SN)_x$ chain appears to consist of, besides the electrons forming the σ bonds which hold it together, a singly occupied π orbital on each S atom, interspersed with a π lone pair centered around each N atom. The polymer may therefore to a good approximation be regarded as a one-dimensional chain of S atoms, with a single electron on each site. This is equivalent to a half-filled band, and consequently one would predict the polymer to be metallic, in agreement with observation.

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