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# On the Singlet Diradical Character of $S_2N_2$

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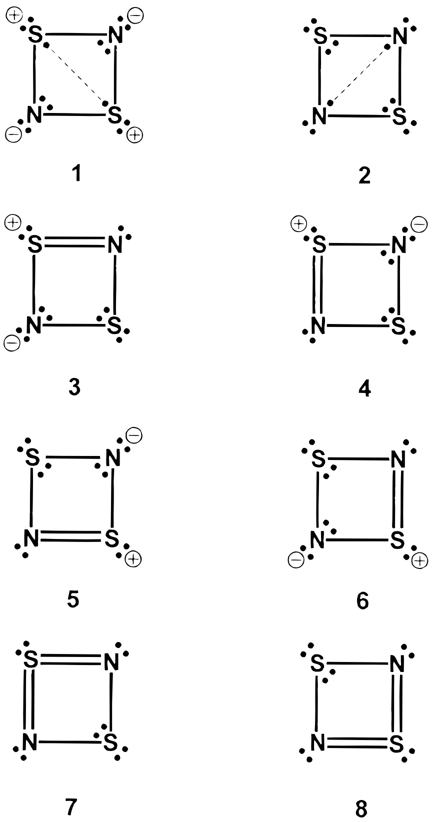
The results of some 6-31G(d) CISD MO calculations for the ground state of cyclic $S_2N_2$ are reported. They give sulfur 3p$\pi$ and nitrogen 2p$\pi$ NAO occupancies of 1.501 and 1.443, respectively. These results are interpreted to indicate that the nitrogen singlet diradical character is larger than the sulfur singlet diradical character. The results of STO-6G valence bond calculations of the energies of the sulfur and nitrogen singlet diradical structures are in accord with this conclusion. However STO-6G CISD calculations give sulfur 3p$\pi$ and nitrogen 2p$\pi$ NAO occupancies of 1.664 and 1.335, respectively, thereby implying that the STO-6G calculations overestimate the extent of nitrogen diradical character. Consideration is given to the use of two equivalent increased-valence structures to provide a valence bond representation of the electronic structure of $S_2N_2$. Regardless of the degree of nitrogen or sulfur singlet diradical character, resonance between these structures, which is equivalent to resonance between the two singlet diradical and four zwitterionic Lewis structures, must provide a lower energy VB represention than does that which is obtained by use of either singlet diradical structure alone.

## Introduction

The results of spin-coupled valence bond (SC-VB) calculations[1] have been used to conclude that the primary VB structure for cyclic $S_2N_2$ resembles the Lewis structure **1** (Chart 1), with alternating positive and negative charges on the sulfur and nitrogen atoms. This structure, with opposed spins for the sulfur $\pi$ electrons, is an example of a singlet diradical structure. A recently published text in inorganic chemistry[2] has referred to this structure and to ref 1. A second $\pi$-electron singlet diradical structure is also possible, namely **2**, in which the odd electrons are located in nitrogen AOs rather than sulfur AOs. The results of some STO-6G VB calculations[3,4] with nonpolar S−N $\sigma$ bonds, and some semiempirical VB calculations,[5] each with 10 Lewis structures included in the resonance scheme,[6] have indicated that structure **2** has a substantially larger weight than has structure **1**, and that the contributions of the zwitterionic Lewis structures **3**−**6** to the ground-state resonance scheme is also substantially larger than that made by structure **1**. Therefore disagreement exists between the conclusions that have been obtained from the results of two ab initio studies. The primary purpose of this paper is to try to ascertain further the relative importance of the two singlet diradical structures. This is achieved partly via the results of CISD MO calculations[7] with both 6-31G(d) and STO-6G basis sets and some additional STO-6G VB calculations.

**CHART 1**



## Results of 6-31G(d) CISD MO Calculations

The natural atomic orbital (NAO)[8,9] occupancies for the CISD 6-31G(d) calculation are reported in Table 1. These occupancies are similar to those that we have obtained from a SCF calculation, which gives the following valence-shell NAO occupancies: N, 2s = 1.689 34, $2p_x = 2p_y = 1.389\,74$, $2p_z = 1.459\,57$; S, 3s = 1.646 86, $3p_x = 3p_y = 0.903\,81$, $3p_z = 1.515\,66$. For the valence-shell orbitals, the Mulliken gross orbital populations[11] obtained from the CISD calculation are N, 2s = 1.813 00, $2p_x = 1.197\,40$, $2p_y = 1.195\,72$, $2p_z = 1.382\,59$; S, 3s = 1.783 41, $3p_x = 0.919\,57$, $3p_y = 0.921\,65$, $3p_z = 1.547\,27$. It is considered that the NAO results are to be preferred.[9]

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**TABLE 1: NAO Occupancies for $S_2N_2$[a]**

| | sulfur | nitrogen | | sulfur | nitrogen |
|---|---|---|---|---|---|
| 1s | 2.0 | 1.999 79 | 4s + 5s | 0.012 68 | 0.000 38 |
| 2s | 1.999 37 | 1.688 01[b] | $4p_x$ | 0.010 46 | |
| $2p_x$ | 1.999 88 | 1.369 64[b] | $4p_y$ | 0.010 33 | |
| $2p_y$ | 1.999 88 | 1.365 79[b] | $4p_z$ | 0.011 79 | |
| $2p_z$ | 1.999 98 | 1.443 09[b] | $3d_{x^2-y^2} + 3d_{z^2} + 3d_{xy}$ | 0.048 36 | 0.027 16 |
| 3s | 1.641 25[b] | 0.003 63 | $3d_{xz} + 3d_{yz}$ | 0.026 82 | 0.014 55 |
| $3p_x$ | 0.901 18[b] | 0.006 89 | | | |
| $3p_y$ | 0.904 23[b] | 0.006 85 | | | |
| $3p_z$ | 1.500 97[b] | 0.008 19 | | | |

[a] The experimental geometry[10] ($d$(S1N2) = 1.651 Å, $d$(N2S3) = 1.657 Å, ∠(S1N2S3) = 90.4°, ∠(N2S3N4) = 89.6°) was assumed. [b] Valence-shell AOs. The $p_z$ AOs are the $\pi$-electron AOs.

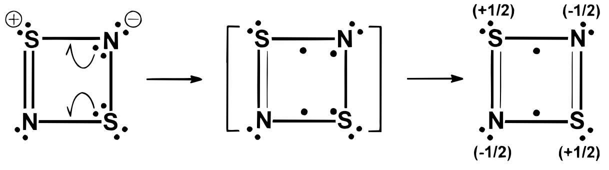
The calculated sulfur and nitrogen NAO net charges[8,9] are $Q_S = +0.932\,83$ and $Q_N = -0.932\,83$, respectively, which would seem to support the conclusion obtained from the spin-coupled calculations that structure **1** could be the primary VB structure. However this conclusion ignores (i) the S−N $\sigma$-bond polarization that occurs for the valence shell $\sigma$ electrons: the total s−p−d populations for these electrons are 3.454 48 and 4.458 82, respectively, and (ii) the values of the valence-shell p$\pi$ AO populations, 1.500 97 (sulfur 3p$\pi$) and 1.443 09 (nitrogen 2p$\pi$). (Inclusion of the Rydberg p$\pi$ AOs of Table 1 changes these p$\pi$ NAO populations only slightly.) Therefore the S−N $\sigma$-bond polarization rather than the $\pi$-electron distribution is primarily responsible for the magnitudes of the atomic net charges. Moreover, the slightly larger 3p$\pi$ population for sulfur suggests that the contribution to the VB resonance scheme of structure **2**, with two 3p$\pi$ electrons per sulfur atom, should be larger than that for structure **1**, with one 3p$\pi$ electron per sulfur atom. This result supports the conclusions obtained from refs 3−5, as well as those obtained from the additional VB calculations that we shall describe below. It is also noted that the CISD and MP2 energies of −904.292 77 and −904.388 06 au are substantially lower than the best spin-coupled energy of −903.912 34 au, which is reported in ref 1. Further comments on energies are provided in the Appendix.

The NAO occupancies for the CISD 6-31G(d) calculation will be used as the benchmark AO occupancies with regard to which the results obtained from STO-6G VB and CISD calculations will be compared. However, prior to consideration of the STO-6G calculations, we give some attention to several types of VB structures for $S_2N_2$.

### Some Comments on Valence Bond Structures

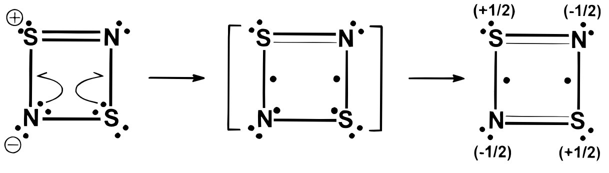
Canonical Lewis structures of types **7** and **8** as well as structure **2** also involve four sulfur 3p$\pi$ electrons. In each of the structures **7** and **8**, a sulfur atom has expanded its valence shell to use either a $d_{xz}$ or a $d_{yz}$ AO as well as a 3p$\pi$ AO, to form simultaneously an electron-pair $\pi$ bond between each of the two nitrogen atoms. However because the NAO populations of the $d_{xz}$ and $d_{yz}$ AOs are so small (Table 1), expanded valence-shell VB structures would be expected to make very minor contributions to the ground-state resonance scheme. Therefore the primary canonical Lewis structures must be structures **1**−**6**, although it may be noted that the AOs that accommodate the six valence-shell $\pi$ electrons will involve small amounts of p$\pi$−d$\pi$ mixing. On numerous occasions,[3,4,12−15] it has been demonstrated that resonance between these six Lewis structures is equivalent to resonance between the increased-valence structures **11** and **14** when the wave functions for the electron-pair $\pi$ bonds are formulated using the Heitler−London procedure, i.e., $(\phi_i, \phi_j) = |\phi_i^\alpha\phi_j^\beta| + |\phi_j^\alpha\phi_i^\beta|$, in which $\phi_i$ and $\phi_j$ are the singly occupied orbitals.

**SCHEME 1**



**9** **10** **11**

**SCHEME 2**



**12** **13** **14**

The increased-valence structures may be derived[3,4,12−15] from the Lewis structures **3**−**6** via the delocalization of one of the lone-pair 3p$\pi$(S) electrons and one of the lone-pair 2p$\pi$(N) electrons in each of these structures, into bonding MOs of the types $\pi$(SN) = 3p$\pi$(S) + $K$2p$\pi$(N) and $\pi$(NS) = 2p$\pi$(N) + $K'$3p$\pi$(S), as is indicated in **9** → **10** → **11** (Scheme 1) and **12** → **13** → **14** (Scheme 2), for example. Because **11** ↔ **14** is equivalent to **1** ↔ **2** ↔ **3** ↔ **4** ↔ **5** ↔ **6**, regardless of which type of canonical Lewis structure is the primary Lewis structure, the increased-valence structures will provide a more complete VB representation when the polarity parameters $K$ and $K'$ in each of the $\pi$(SN) and $\pi$(NS) MOs are chosen variationally. Relationships that exist between MO-CI wave functions, and the relevance of such structures for VB representations of $S_2N_2$ polymerization and electron conduction in the polymer $(SN)_x$, are provided in refs 3, 4, and 12−15.

From the properties of the spin-coupled orbitals $\phi_1$ and $\phi_2$ of ref 1, it is concluded[1] that structure **1** does not involve an S−S $\pi$ bond. However if the ($\phi_1$, $\phi_2$)($\phi_3$, $\phi_4$)($\phi_5$, $\phi_6$) spin-coupled configuration of ref 1 is expanded as a linear combination of $S = 0$ spin AO configurations, the wave functions for the 10 canonical Lewis structures of refs 3−5 (together with other structures, such as **7** and **8** here, for example) will contribute to the linear combination. Each of the canonical structures **1** and **2** involves the spin pairing of electrons that singly occupy (weakly) overlapping sulfur or nitrogen p$\pi$ AOs, and therefore "long" or formal or secondary S−S or N−N bonds (with negligible strengths) will be formed in these structures. In ref 16, further comments with regard to the interpretation of the results of SC-VB calculations are provided.

### Valence Bond Calculations

Although it is probable that STO-6G VB calculations overestimate the degree of nitrogen diradical character, we have examined further the relative importance of structures **1** and **2**, via some additional VB calculations that are based on the procedure described in ref 3. Because each of these structures may be converted into one of the zwitterionic structures **3**−**6** via a one-electron transfer (either $N^-(2p\pi) \rightarrow S^+(3p\pi)$ or $S(3p\pi) \rightarrow N(2p\pi)$), Hamiltonian matrix elements of the types $\langle\Psi_1|H|\Psi_3\rangle$ and $\langle\Psi_2|H|\Psi_3\rangle$ should have similar magnitudes for normalized $\Psi_i$, as should the corresponding overlap integrals $\langle\Psi_1|\Psi_3\rangle$ and $\langle\Psi_2|\Psi_3\rangle$. Therefore, the relative extent to which structures **1** and **2** interact with structures **3**−**6** will depend primarily on the energies of structures **1** and **2**. We have calculated these energies using several sets of AOs.

**TABLE 2: Energies ($E$, au, Experimental Geometry[10]) and S−N $\sigma$-Bond Polarity Parameter $k$ for Canonical Lewis Structures 1 and 2**

| calculation | $E + 900.0$ | $k$ | calculation | $E + 900.0$ | $k$ |
|---|---|---|---|---|---|
| a | −0.915 68 | 0.6 | f | −0.977 87 | 1.0 |
| b | −0.934 78 | 0.9 | g | −1.071 18 | 1.0 |
| c | −0.942 22 | 0.9 | h | −1.072 11 | 1.0 |
| d | −1.048 42 | 0.9 | a | −1.191 71[a] | 1.1 |
| e | −1.054 80 | 0.9 | a | −0.935 87[a] | 0.6 |

[a] Structure **2**.

The calculations have been performed using Roso's ab initio VB program.[3,4,17] Allowance has been made for polarization of the S−N $\sigma$-bonds via $\sigma(\mathrm{SN}) = h_\mathrm{N} + kh_\mathrm{S}$. The values of the s−p hybridization parameters ($\lambda$ in $h = p + \lambda s$) for the $h_\mathrm{S}$ and $h_\mathrm{N}$ AOs have been assumed to be the same as those obtained from the calculations of ref 3, namely 0.255 and 0.2025, respectively. Initially (calculations (a) of Table 2) single-$\zeta$ "best atom" exponents[3,18] were used for both structures. Energies of −900.915 68 and −901.191 71 au (Table 2) are thereby obtained for these two structures. To improve the energy of structure **1**, a variety of calculations were then performed using the following sets of AO exponents.

(b) Single-$\zeta$ "best atom" for the s AOs of $\mathrm{N}^-$ and $\mathrm{S}^+$ and the 2p AO of $\mathrm{S}^+$, and single-$\zeta$ "best ion" for the valence-shell p AOs of $\mathrm{N}^-$ and $\mathrm{S}^+$.

(c) Single-$\zeta$ "best ion" for all of the AOs of $\mathrm{S}^+$ and the 2p AOs of $\mathrm{N}^-$, single-$\zeta$ "best atom" for the 1s AO of $\mathrm{N}^-$, and a variationally determined value of 2.0 for the 2s exponent of $\mathrm{N}^-$.

(d) As for (b), but with the double-$\zeta$ 2p$\pi$($\mathrm{N}^-$) AO of ref 19, namely, $2\mathrm{p}\pi(\mathrm{N}^-) = 2\mathrm{p}\pi(\zeta' = 0.870\,621) + \kappa 2\mathrm{p}\pi(\zeta'' = 2.414)$, with $\kappa = 1.0098$.

(e) As for (d), but with $\kappa = 1.2$ determined variationally.

(f) As for (d), but with $2\mathrm{p}\pi(\zeta' = 0.870\,621)$ and $2\mathrm{p}\pi(\zeta'' = 2.414)$ chosen to accommodate the pair of 2p$\pi$ electrons for each $\mathrm{N}^-$.

(g) As for (f), but with $\zeta' = 1.1$ determined variationally.

(h) As for (g), but with $\zeta'' = 2.3$ determined variationally when $\zeta' = 1.1$. Because only a small decrease in the energy was obtained, the value of 1.1 for $\zeta'$ was not reoptimized.

For each of the calculations of (a)−(d), there are two singly occupied AOs, and the $S = 0$ spin wave function for the associated electrons is of the Heitler−London type $(\phi_i, \phi_j) = |\phi_i^\alpha \phi_j^\beta| + |\phi_j^\alpha \phi_i^\beta|$. Each of the calculations of (f)−(h) involves six singly occupied $\pi$-electron orbitals, as there are in ref 1. The appropriate $S = 0$ spin wave function for the resulting six-orbital $(\phi_1, \phi_2)(\phi_3, \phi_4)(\phi_5, \phi_6)$ configuration may be developed from $(\phi_i, \phi_j)$ and corresponds to that which is presented in ref 20, for example. Results of all calculations, with variationally determined values for the polarity parameter $k$ for the S−N $\sigma$ bonds, are reported in Table 2.

Each of the calculations for (b)−(h) improves the energy of structure **1** relative to that calculated with "best atom" exponents, but in no case does the energy of sulfur singlet diradical structure **2** approach that for the single-$\zeta$ "best atom" calculation for the nitrogen singlet diradical structure **2**.

We note that except for the calculation of (a), the S−N $\sigma$-electron polarization parameter $k$ has a value near 0.9 for structure **1**, thereby implying that these bonds are rather less polarized in the sense S → N than they are for each of the CISD and SC-VB[1] calculations with 6-31G(d) and DZP bases, respectively. In the calculations of (a) for structures **1** and **2**, the $\sigma$-bond polarity parameter has values of 0.6 and 1.1, respectively. When $k = 0.6$ for structure **2**, the energy of this structure (−900.935 87 au) still lies slightly below the −900.915 68 au for structure **1**.

**TABLE 3: STO-6G CISD NAO Occupancies for $S_2N_2$[a]**

| | sulfur | nitrogen | | sulfur |
|---|---|---|---|---|
| 1s | 2.0 | 1.999 99 | 3s | 1.806 71[b] |
| 2s | 1.999 97 | 1.798 50[b] | 3p$_x$ | 1.055 86[b] |
| 2p$_x$ | 1.999 98 | 1.142 26[b] | 3p$_y$ | 1.059 64[b] |
| 2p$_y$ | 1.999 98 | 1.137 54[b] | 3p$_z$ | 1.664 27[b] |
| 2p$_z$ | 1.999 98 | 1.335 33[b] | | |

[a] The experimental geometry[10] was assumed. [b] Valence-shell AOs. The p$_z$ AOs are the $\pi$-electron AOs.

## STO-6G CISD Calculations

With an STO-6G basis, we have also performed some CISD calculations (Table 3). In accord with the results of the STO-6G VB calculations, these CISD calculations also indicate less S → N polarization for the S−N $\sigma$ bonds than do the CISD 6-31G(d) calculations. As a consequence, the STO-6G S(3p$\pi$) and N(2p$\pi$) NAO occupancies of 1.664 and 1.335 are respectively appreciably larger and smaller than the 1.501 and 1.443 obtained with the 6-31G(d) basis (Table 1). The magnitude of the STO-6G net charges ($Q_\mathrm{S} = -Q_\mathrm{N} = +0.413\,63$) is much smaller than that for the 6-31G(d) net charges ($Q_\mathrm{S} = -Q_\mathrm{N} = +0.932\,83$). However, although the STO-6G CISD and the VB calculations both appear to overestimate the importance of structure **2** relative to structure **1**, the conclusion obtained from these calculations that the ground-state singlet diradical character of $S_2N_2$ involves a larger nitrogen than sulfur contribution is in accord with the deduction that has been made from the results of the CISD MO calculations with the 6-31G(d) basis. But because a substantial difference does not exist between the 6-31G(d) NAO occupancies for the sulfur 3p$\pi$ and the nitrogen 2p$\pi$ AOs, the conclusion must be considered to be provisional. The bond-index studies reported in ref 21 have been considered to provide inconclusive evidence with regard to the relative importance of the sulfur and nitrogen singlet diradical character.

One other comment may be made with regard to the spin-coupled calculations, as described in ref 1. Because only one set of six orbitals is used, the symmetry of the molecule means that these orbitals can only resemble those for either structure **1** or structure **2**. Twenty-four spin-coupled orbitals would be required to describe resonance between four structures that resemble structures **3**−**6**. This possibility has not been considered in ref 1.

## Conclusions

Although the results of our calculations suggest that the singlet diradical character of $S_2N_2$ is associated more with the nitrogen atoms than with the sulfur atoms and therefore VB structure **2** is more important than VB structure **1**, it is probable that the jury is still out with regard to which of these two structures is the primary singlet diradical structure. However, because resonance between the increased-valence structures **11** and **14** is equivalent to resonance between the Lewis structures **1**−**6**, it is a truism to say that the **11** ↔ **14** resonance provides the better VB representation than do either of the singlet diradical structures alone.

**Note Added in Proof.** Spin-coupled VB energies for structures **2** and **7** ↔ **8** as well as for structure **1** have now been reported (Thorsteinsson, T.; Cooper, D. L. *J. Math. Chem.* **1998**, in press). The SC energies for **1** and **7** ↔ **8** are similar and lie below those of **2**. A SC energy for resonance between the increased-valence structures **11** and **14** has yet to be

**TABLE 4: Energies ($E$, au) for $S_2N_2$ Calculated with ($a$) Experimental Geometry[10] and ($b$) Idealized Geometry[1] (Square, with $d$(SN) = 1.654 Å)[c]**

| | present work, 6-31G(d) basis | | ref 1, DZP basis | |
|---|---|---|---|---|
| | $E + 903.0$ | $E + 903.0$ | | $E + 903.0$ |
| HF | $-0.766\ 73^a$ | $-0.641\ 99^b$ | HF | $-0.784\ 34^b$ |
| MP2 | $-1.388\ 06^a$ | $-1.219\ 28^b$ | "best" SC | $-0.912\ 34^b$ |
| CISD | $-1.292\ 77^a$ | | | |

[c] The STO-6G CISD energy, for the experimental geometry, is −900.933 27 au.

determined. We thank Professor Cooper for providing us with a preprint of his paper.

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## Appendix

In Table 4, we report energies obtained using (a) the experimental geometry of ref 10 and (b) the idealized geometry of ref 1. The values of the Hartree−Fock (HF) energies show that the DZP basis set used to obtain the energies reported in Table 1 of ref 1 is slightly superior to the 6-31G(d) basis used in the present work. However, when correlation is introduced−either via MP2 or CISD−the 6-31G(d) calculations generate energies that are substantially lower than the "best" SC-VB energy reported in Table 1 of ref 1.

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