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Ab Initio Double-ζ (D95) Valence Bond Calculations for the Ground States of S_2N_2 and S_4^{2+}

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The results of double-ζ D95 valence-bond (VB) calculations are reported for the ground states of S_2N_2 and S_4^{2+}. The Mulliken, Löwdin, and Hiberty structural weights are reported for ten Lewis structures that differ in the locations of six π electrons. The most important Lewis structure for S_2N_2 is the nitrogen singlet diradical structure (**I**) with a structural weight of 0.47. For S_4^{2+} the two singlet diradical structures (**XI** and **XII**) with structural weights of 0.23 each are by far the most important individual Lewis structures.

Introduction

The geometry of the two molecules S_2N_2 and S_4^{2+} is almost exactly that of a square (Table 1), which is also in accord with the results of high-level density functional theory molecular orbital (DFT-MO) calculations (Table 1). Especially for S_2N_2 the bonding situation is far from obvious. Whereas an early semiempirical INDO study[5] and the results of a single-ζ (STO-6G) ab initio valence bond (VB) calculation[6a,b] indicate that the primary Lewis VB structure is a nitrogen singlet diradical (or "long-bond") structure (**I**, Figure 1), the results of spin-coupled VB (SC-VB) calculations[7a,b] have been used to conclude that the primary VB structure for cyclic S_2N_2 resembles Lewis structure **II** (Figure 1), which is a sulfur singlet diradical (or "long-bond") structure with alternating positive and negative charges on the sulfur and nitrogen atoms. In contrast to the latter findings, in a more recent paper, the results of double-ζ (6-31G(d)) CISD MO calculations have been interpreted to indicate that the nitrogen singlet diradical character is larger than the sulfur diradical character.[8] Naturally no quantitative structural weights could be obtained from the MO calculations, and the most recent paper on this topic concludes, "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 ..., it is probable that the jury is still out with regard to which of these two (**I** or **II**) structures is the primary singlet diradical structure".[8]

The results of single-ζ (STO-6G)[6b,9] calculations also indicate that singlet diradical Lewis structures (namely structures **XI** and **XII** of Figure 2) are the primary types of Lewis structures for S_4^{2+}.

Here we report on the results of ab initio VB calculations for S_2N_2 and S_4^{2+} using Dunning's D95 full double-ζ basis set. For each molecule, S_2N_2 and S_4^{2+}, weights were calculated for the ten $S = 0$ VB structures of Figures 1 and 2 that differ in the distribution of six π electrons among four valence-shell p_π atomic orbitals (AOs). Because the populations of the d AOs are generally very small,[8] expanded valence-shell structures would be expected to make very minor contributions to the ground state resonance scheme and have therefore been omitted.

TABLE 1: Structural Parameters of S_2N_2 and S_4^{2+}

	S_2N_2	S_4^{2+}
d/Å, X-ray	1.657(1)−1.651(1)	1.924(4)−2.023(3)
d/Å, DFT[a]	1.6418	2.0253
∠(SNS)/deg, X-ray	90.4(1)	
∠(SNS)/deg, DFT[a]	89.1	
∠(NSN)/deg, X-ray	89.6(1)	
∠(NSN)/deg, DFT[a]	90.9	
∠(SSS)/deg, X-ray		87.9(2)−92.5(2)
∠(SSS)/deg, DFT[a]		90.0

[a] MPW1PW91/cc-pVTZ.

Method

The VB program package VB2000, version 1.7 (running under LINUX), was used for all VB calculations employing a full D95 double-ζ basis set.[10−17] VB2000 is an ab initio electronic structure package for performing modern VB calculations; it is based on a highly efficient VB algorithm (the so-called algebrant algorithm[11,12]) and the group function (GF) approach,[13−15] in which a large molecule is described in terms of its constituent parts, physically identifiable "electron groups". A major feature of VB2000 is the implementation of modern VB theory at ab initio level using the algebrant algorithm. The VB method used in this study was the *multistructure VB* method implemented in the VB2000 program package, which generates the weights of all resonance structures. In VB2000 each "structure" becomes a spin-coupling scheme, involving pairs of electrons occupying rather localized, strongly overlapping orbitals.

For each of S_2N_2 and S_4^{2+}, a VB(6)/D95 calculation with six π electrons was performed. The σ and inner-shell π electrons were accommodated in Hartree−Fock SCF MOs. With these cores ($S = 0$ spin) VB calculations were performed for the six π electrons that differ in their locations in Figures 1 and 2. The orbitals that were used to accommodate the π electrons were determined via the variational mixing in the 10 structure calculations of all π-type symmetry basis functions which arise in the D95 double-ζ (or larger) basis sets. These orbitals were calculated to be primarily one-center AOs with only a very small degree of "tailing", i.e., spreading onto other atomic centers (cf. Table 2).

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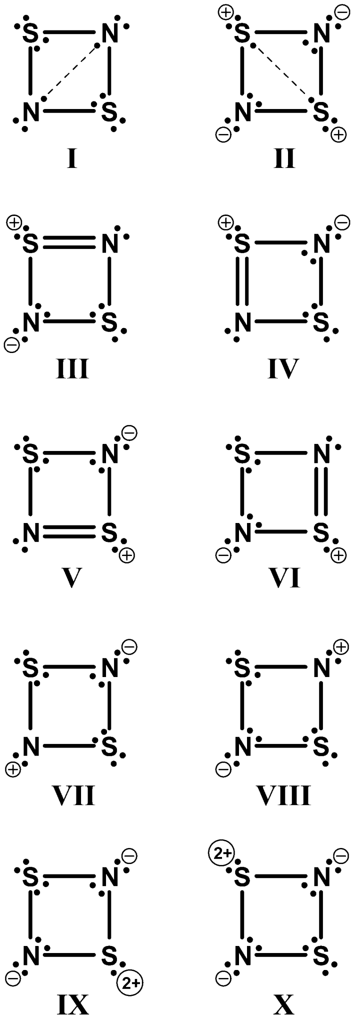

Figure 1. Singlet diradical structures **I** and **II**, zwitterionic Kekulé structures **III**−**VI**, and "co-ionic" structures **VII**−**X** for S_2N_2.

The molecules were assumed to possess D_{2h} (S_2N_2) and D_{4h} (S_4^{2+}) symmetries with bond lengths of 1.642 (S_2N_2) and 2.025 Å, respectively.

The MPW1PW91/cc-pVTZ calculations for S_2N_2 and S_4^{2+} (cf. Table 1) were performed with the program package Gaussian 98.[18]

The weights for the VB structures were calculated according to the Mulliken (Chirgwin−Coulson),[19a] Löwdin,[19b] and Hiberty[19c−f] procedures, namely (a) $W_i = \sum_j C_j C_i S_{ij}$ (where C_i and C_j are the coefficients of the wave functions for VB structures i and j, respectively, and S_{ij} is the overlap integral for the wave functions for these structures), (b) $W_i = (C'_i)^2$ (where C'_i is the coefficient of the orthogonalized wave function for structure i), and (c) $W_i = C_i^2/\sum C_i^2$.

Results and Discussion

Tables 3 and 4 summarize the computed normalized C_i coefficients and structure weights for the 10 VB structures for S_2N_2 and S_4^{2+}. As can be seen from Tables 3 and 4, though somewhat different, in general, the Mulliken-, Löwdin-, and Hiberty-type structural weights reflect the same trend.

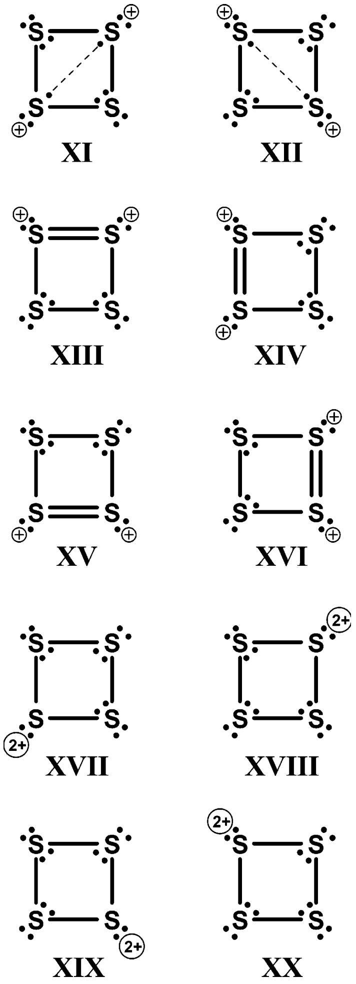

Figure 2. Singlet diradical structures **XI** and **XII**, Kekulé structures **XIII**−**XVI**, and "co-ionic" structures **XVII**−**XX** for S_4^{2+}.

The calculated structural weights for S_2N_2 indicate clearly that the primary Lewis VB structure is the nitrogen singlet diradical (or Dewar or "long-bond") structure **I**. This structure has substantially larger weight than has the other Dewar-type structure **II**, which represents the sulfur singlet diradical structure. The contribution of each of the four zwitterionic Lewis structures **III**−**VI** to the ground state resonance scheme is also substantially larger than that made by structure **II**. The four "co-ionic" structures **VII**−**X** have quite small weights with the structures **VII** and **VIII** which have one positive and one negative nitrogen atom being slightly more important than structures **IX** and **X** with two negative nitrogen atoms and one doubly positively charged sulfur atom. These results agree well with earlier findings by Fujimoto[5] and Harcourt et al.;[6,8,9] however, they do not support the conclusion of Gerratt et al.[7] that the primary VB structure for S_2N_2 resembles Lewis structure **II**. Moreover, the results presented in this contribution are also in good accord with "chemical intuition" that the Lewis structure with the maximum number of bonds and the minimum number of atomic formal charges should be the most important Lewis-type structure. In the case of S_2N_2, structure **I** is the only structure without formal charges.

Further support for the preference of structure **I** over structure **II** is provided by the results of our GVB(2) calculations with a D95 basis set.[18] The energies of these structures are −903.582489 and −903.543118 au, respectively, to indicate that structure **I** is stabilized by 24.69 kcal mol^{-1} relative to structure **II**.

For the S_4^{2+} dication the two equivalent singlet (or "long-bond") diradical VB structures **XI** and **XII** are the primary Lewis VB structures (Table 3). The four equivalent Kekulé structures **XIII**−**XVI** with a π bond between two adjacent sulfur atoms also contribute significantly to the ground state resonance scheme whereas the weights of the four equivalent "co-ionic"

TABLE 2: AO Coefficients for the Valence-Shell π-Electron Orbitals of S_2N_2 and S_4^{2+}

valence-shell π-electron orbital		sulfur	nitrogen
	S_2N_2		
S1	$2p_{x,1}'$	−0.248	0.004
	$2p_{x,1}''$	−0.028	−0.002
	$3p_{x,1}'$	0.572	−0.020
	$3p_{x,1}''$	0.571	−0.080
N2	$2p_{x,2}'$	−0.067	0.806
	$2p_{x,2}''$	−0.004	0.357
N3	$2p_{x,3}'$	−0.067	0.085
	$2p_{x,3}''$	−0.004	−0.062
S4	$2p_{x,4}'$	0.003	0.004
	$2p_{x,4}''$	−0.001	−0.002
	$3p_{x,4}'$	0.009	−0.020
	$3p_{x,4}''$	0.038	−0.080
	S_4^{2+}		
S1	$2p_{x,1}'$	−0.258	
	$2p_{x,1}''$	−0.030	
	$3p_{x,1}'$	0.618	
	$3p_{x,1}''$	0.522	
S2	$2p_{x,2}'$	0.012	
	$2p_{x,2}''$	0.000	
	$3p_{x,2}'$	−0.051	
	$3p_{x,2}''$	−0.026	
S3	$2p_{x,3}'$	0.012	
	$2p_{x,3}''$	0.000	
	$3p_{x,3}'$	−0.051	
	$3p_{x,3}''$	−0.026	
S4	$2p_{x,3}'$	−0.007	
	$2p_{x,1}''$	−0.001	
	$3p_{x,1}'$	0.026	
	$3p_{x,1}''$	−0.025	

TABLE 3: Normalized C_i Coefficients and Weights (Mulliken, Löwdin, and Hiberty Types) for S_2N_2 Using a D95 Basis Set

structure, i	coefficient, C_i	Mulliken structure weight, $W_{i,M}$	Löwdin structure weight, $W_{i,L}$	Hiberty structure weight, $W_{i,H}$
I	0.6758	0.47	0.47	0.47
II	0.2281	0.06	0.06	0.06
III	−0.3040	0.10	0.10	0.10
IV	−0.3040	0.10	0.10	0.10
V	−0.3040	0.10	0.10	0.10
VI	−0.3040	0.10	0.10	0.10
VII	−0.1644	0.02	0.02	0.03
VIII	−0.1644	0.02	0.02	0.03
IX	−0.0936	0.01	0.01	0.01
X	−0.0936	0.01	0.01	0.01

structures **XVII**−**XX** for S_4^{2+} are comparatively low. The calculated weights are in close accord with those obtained from single-ζ STO-6G VB calculations.[6b,9]

Although the aim of this paper is to focus on standard (Kekulé-type and Dewar-type) Lewis VB structures, it should be mentioned that on numerous occasions[6,8,9,20,21] it has been demonstrated that resonance between the six most important Lewis structures (**I**−**VI**; **XI**−**XVI**) is equivalent to resonance[22] between the increased-valence structures **XXI** and **XXII** (for S_2N_2) and **XXIII** and **XXIV** (for S_4^{2+}) (Figure 3). The use of the increased-valence structures for S_2N_2 to provide a VB representation for the $S_2N_2 \rightarrow (SN)_x$ polymerization is provided in refs 6 and 20c. In general, increased-valence structures for cyclic six-electron four-center bonding units are discussed in refs 6, 8, 9, 20, 21, and 23.

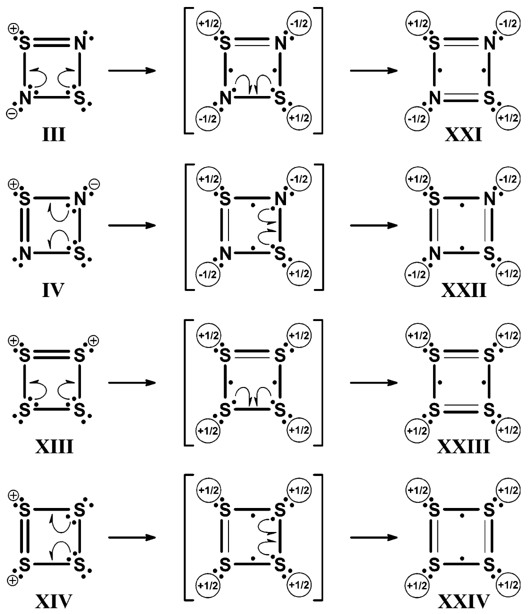

Figure 3. Derivation of increased-valence structures for S_2N_2 (**XXI** and **XXII**) and for S_4^{2+} (**XXIII** and **XXIV**).

TABLE 4: Normalized C_i Coefficients and Weights (Mulliken, Löwdin, and Hiberty Types) for S_4^{2+} Using a D95 Basis Set

structure, i	coefficient, C_i	Mulliken structure weight, $W_{i,M}$	Löwdin structure weight, $W_{i,L}$	Hiberty structure weight, $W_{i,H}$
XI	−0.4710	0.23	0.26	0.23
XII	−0.4710	0.23	0.26	0.23
XIII	0.3390	0.12	0.12	0.12
XIV	0.3390	0.12	0.12	0.12
XV	0.3390	0.12	0.12	0.12
XVI	0.3390	0.12	0.12	0.12
XVII	0.1192	0.02	0.01	0.01
XVIII	0.1192	0.02	0.01	0.01
XIX	0.1192	0.02	0.01	0.01
XX	0.1192	0.02	0.01	0.01

Aromaticity and Some Other Properties of S_2N_2

Since completing work, we have received a paper[24] on the aromaticity of S_2N_2. Aspects of ref 24 can be compared with the point of view expressed in the VB studies of refs 6 and 8, in which it has *not* been claimed that S_2N_2 is a singlet diradical. In ref 6a it has been calculated that

(a) The most important *Lewis*-type VB structure is the singlet diradical structure **I**, but it is recognized fully that the zwitterionic Lewis structures **III**−**VI** (or **1**−**4** of ref 6a, or **4**−**7** of ref 24) contribute significantly to the ground state resonance of the electronic structure.

(b) An STO-6G VB estimate of the singlet−triplet energy separation (E(**I**−**VI**, S=1) − E(**I**−**X**, S=0)) is 1.6 eV; cf. 3.6 eV.[24] We have subsequently calculated an STO-6G estimate of 0.1 eV for E(**I**,S=1) − E(**I**,S=0), i.e., for S_2N_2 as a nitrogen diradical. (The singlet nitrogen diradical structure **I** is calculated to be stabilized by 0.2 eV through resonance with structures **VII** and **VIII**.)

(c) An STO-6G VB estimate (E(**I**,**III**−**VI**, S=1) − E(**III**−**X**, S=0) is −2.81 eV; i.e., it is calculated that Lewis structure **I** needs to be included in the ground state resonance scheme to stabilize the singlet-spin state relative to the triplet-spin state.

Also, in ref 6a, it is indicated that the $(1b_{1u})^2(1b_{3g})^2(1b_{1g})^2$ MO configuration disguises the contribution of **I** (and also **II**−**X**) to the equivalent VB resonance scheme.[25] In ref 20b an analysis of the three-configuration MO wave function $C_1(1b_{1u})^2(1b_{3g})^2(1b_{2g})^2 + C_2(1b_{1u})^2(1b_{3g})^2(2b_{1u})^2 + C_3(1b_{1u})^2(1b_{2g})^2(2b_{1u})^2$ is provided,[26] to show that resonance between the increased-valence structures **XXI** and **XII** provides the primary VB description of the ground state of S_2N_2.

In ref 24, estimates of −0.7 and 6.5 kcal mol^{-1} are provided for the aromatic stabilization energy (ASE) for S_2N_2 (cf. ASE = 33 kcal mol^{-1} for C_6H_6).[24] Here we assume that the ΔE values, E(localized) − E(delocalized) for both S_2N_2 and C_6H_6 is proportional to the ASE. With the geometries for E(delocalized), the ΔE values were calculated from E(**III**,**VIII**,**X**) − E(**I**−**X**) for S_2N_2 (r(SN) = 1.642 Å) and E(Kekulé) − E(delocalized) for C_6H_6 (r(C−C) = 1.39 Å). For C_6H_6, all canonical Lewis structures that do not involve any of $C^+{-}C^+$, $C^-{-}C^-$, $C^+{-}C^+{-}C^+$, and $C^-{-}C^-{-}C^-$ were included in the calculations. There are respectively 15 and 55 such structures for E(Kekulé) and E(delocalized). We thereby calculate values of 2.1 and 10.5 kcal mol^{-1} for the ΔE of S_2N_2 and C_6H_6. Therefore, in agreement with Schleyer et al.,[24] S_2N_2 is calculated to be weakly aromatic, when we assume that the ΔE is proportional to the ASE.

Finally, in ref 24, it is indicated that a two-electron four-center bond is associated with the (primary) MO configuration, and that resonance between the Lewis structures **III**−**VI** gives an average S−N bond order of 1.25. When (for illustrative purposes here) the electrons that form the one-electron S−N π bonds of increased-valence structures **XXI** and **XXII** are assumed to be shared equally between the S and N atoms, two of the S−N bonds in each increased-valence structure have “bond orders” of 1.5, and two of them have S−N “bond numbers” of 1.25 (cf. refs 20 and 21). The average S−N “bond character” is then 1.375.

Conclusions

From the present ab initio VB study for the ground states of S_2N_2 and S_4^{2+} the following conclusions can be drawn:

(i) The question as to whether the nitrogen (**I**) or sulfur singlet diradical structure (**II**) is the primary VB structure for S_2N_2 can clearly be answered in favor of the nitrogen singlet diradical (or “long-bond”) structure **I** with a structural weight of 0.47.

(ii) For the S_4^{2+} dication the two equivalent sulfur···sulfur singlet diradical structures **XI** and **XII** are by far the most important Lewis structures with structural weights of 0.23 each.

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Appendix. Some Properties of Spin-Coupled (SC) Wave Functions for S_2N_2

The SC orbitals of ref 7 that are used to accommodate the π electrons are not one-center AOs, but are “distorted” AOs which involve AO contributions from two or more atomic centers. Thus, the SC π-electron orbitals of Figure 1 of ref 7a have the approximate forms that are given by eq 1 (cf. ref 27):

$$\begin{aligned}\varphi_1 &= a' + \lambda c'\\ \varphi_2 &= c' + \lambda a'\\ \varphi_3 &= a'' + c'' + \mu d'\\ \varphi_4 &= a''' + c''' + \nu d''\\ \varphi_5 &= a''' + c''' + \nu b''\\ \varphi_6 &= a'' + c'' + \mu b'\end{aligned} \qquad (1)$$

in which λ, μ, and ν are variational parameters. a′, a″, and a‴, and c′, c″, and c‴ are equivalent to sulfur π-electron AOs located on the two sulfur centers. Similarly b′, b″, d′, and d″ are nitrogen π-electron AOs. (With, for example, a double-ζ basis set, the extent of mixing of the double-ζ components varies in the orbitals labeled by ′, ″, and ‴.) With the (φ_1, φ_2), (φ_3, φ_4), and (φ_5, φ_6) spin pairings of ref 7a, the SC wave function can be expressed as a linear combination of the wave functions for the 10 canonical Lewis structures of Figure 1. A knowledge of the values for the λ, μ, and ν parameters is needed to determine the weights for the 10 canonical Lewis structures that are associated with the SC wave functions. However, because there are five distinct types of Lewis structures in Figure 1, the SC estimates of their weights, via the three λ, μ, and ν parameters, will not correspond to the variationally best estimates of their weights.

Note Added in Proof

For recent MO studies of S_2N_2 and S_4^{2+}, see:

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(22) If Coulson−Fischer localized MOs (for example, $\pi(\mathrm{SN}) = \mathrm{a} + k'\mathrm{b}$) rather than AOs are used to accommodate the electrons that form the (fractional) electron-pair S−N or S−S π bonds in the increased-valence structures **XXI**−**XXIV**, then the wave function for resonance between a pair of increased-valence structures involves four independent variational parameters (k', k'', l', and l''). When these parameters are chosen variationally, resonance between the associated pair of increased-valence structures is equivalent to resonance between the 10 Lewis structures of Tables 2 and 3.

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(25) In ref 20b, it is deduced that $(1b_{1u})^2(1b_{3g})^2(1b_{2g})^2 = \Phi$(covalent) + Φ(ionic). Φ(covalent) corresponds to the wave function for resonance between the increased-valence structures **XXI** and **XXII**, which together are equivalent to resonance between the Lewis structures **I**−**VI**. With $1b_{1u} = \mathrm{a} + k\mathrm{b} + \mathrm{c} + k\mathrm{d}$ (a and c are the sulfur AOs), $k = 0$, 1, and ∞ generate weights of 1.0, 0.25, and 0 for the singlet diradical structure **I**, 0, 0.125, and 1.0 for the singlet diradical structure **II**, and 0, 0.5, and 0 for the zwitterionic structures **III**−**VI** together in the Φ(covalent) component of $(1b_{1u})^2(1b_{3g})^2(1b_{2g})^2$.

(26) The $S = 0$ configurations $(2b_{1u})^2(1b_{3g})^2(1b_{2g})^2$ and $(1b_{1u})^1(2b_{1u})^1(1b_{3g})^2(1b_{2g})^2$ need also to be included so that, for the same AO basis, the resulting five-configuration MO wave function is equivalent to the variationally best VB wave function for resonance between 10 Lewis structures.

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