# Ab Initio Valence Bond Calculations and the Spin-Paired Diradical Character of S_2N_2

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Abstract: The results of STO-6G valence bond calculations for S_2N_2, with sulfur 3d orbitals omitted, support a conclusion obtained from a previous INDO study, namely that the primary Lewis valence bond structure is a spin-paired diradical (or "long-bond") structure. If this structure is excluded from the set of $S = 0$ Lewis structures, the ground state is calculated to be an $S = 1$ spin state. "Increased-valence" structures are used to provide qualitative valence bond mechanisms for the thermal polymerization of S_2N_2 to $(SN)_x$ and electron conduction in $(SN)_x$.

When sulfur 3d orbitals are omitted from the bonding scheme for S_2N_2, it is usually assumed that the zwitterionic Lewis structures **1–4**
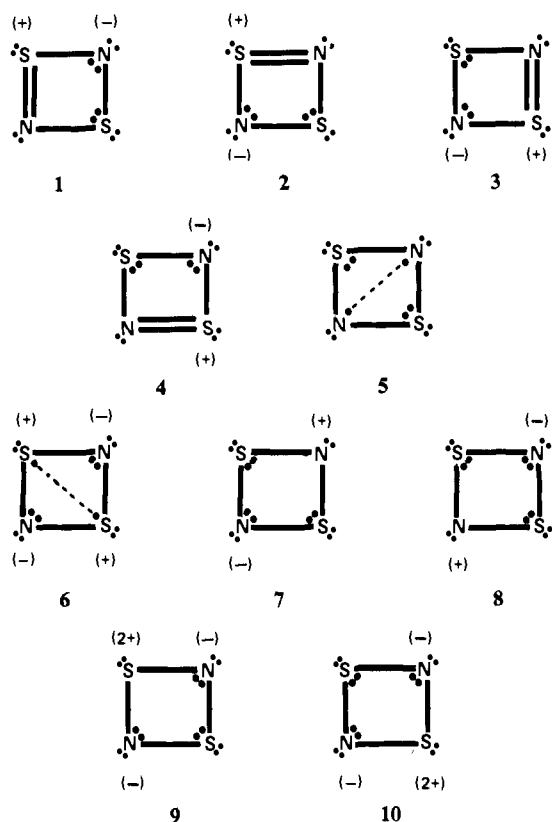
are the primary structures required to provide a qualitative VB description for this molecule. No consideration is given to the possibility that there may be an appreciable contribution from the spin-paired diradical or "long-bond" structure[1] (**5**) to the ground-state resonance. However, an INDO VB calculation[3] (Table I) gives a much larger weight for **5** than it does for the sum of the weights for structures **1–4**. No other VB study has been reported. Here we shall describe the results of some ab initio STO-6G[4] VB calculations; these support the INDO finding.

Method

The $S = 0$ VB structure functions (or bond eigenfunctions) were of the general type $|...\phi_\mu\bar{\phi}_\nu| + |...\phi_\nu\bar{\phi}_\mu|$ for each of the (Lewis) structures **1–6** with a $\phi_\mu-\phi_\nu$ π-bond and $|...\phi_\mu\bar{\phi}_\mu|$ for each of the structures **7–10**. In order to restrict the number of Slater determinants per bond eigenfunction to either one or two, we have located the eight electrons of the four S–N σ-bonds in four two-center bonding MO's of the general form $\sigma_{SN} = h_N + h_S$, with $h_N = (2p_N + \lambda_N 2s_N)/(1 + \lambda_N^2)^{1/2}$, $h_S = (3p_S + \lambda_S 3s_S)/(1 + \lambda_S^2)^{1/2}$, $np \equiv np_y$ or np_z, and no inner-shell valence-shell hybridization. All remaining electrons were located in doubly-occupied AO's, four of which were valence-shell hybrid orbitals orthogonal to the above h_N or h_S on the same atomic center. The $2p\pi_N$ and $3p\pi_S$ were assigned the following values for the orbital exponents in separate calculations: (a) "best atom"[5] and (b) "best atom" and "best ion"[5] for the N, N⁻, S, and S⁺ of structures **1–10**, namely 1.9171, 1.6738, 1.8270, and 1.9676. "Best atom" exponents[5] were used for the remaining 24 s and p AO's. With 90° bond angles and $r(SN) = 1.654$ Å,[6] the VB calculations were performed by using the ab initio VB program initially prepared by Roso,[7] which one of us (F.L.S.) has redimensioned beyond that described previously.[7] The VB weights, which were calculated by using the Chirgwin and Coulson formula,[8] are reported in Table I, together with the energies for different values of the hybridization parameters λ_N and λ_S.

Results

The two calculations with no s–p hybridization show that the VB weight for structure **5** in particular, is rather sensitive to the values of the orbital exponents, with the exponents of (b) giving the lower energy for the ten-structure resonance. Because no VB structures were included to allow for polarization of the S–N σ-bonds and inner-shell valence-shell hybridization, it is perhaps not surprising that the VB energies are higher than the corresponding STO-6G MO energies of –901.3618 au (RHF for $S = 0$) and –901.4028 au (UHF for $S = 1$), which we have calculated by using best atom exponents and the GAUSSIAN 80 program.[9] The RHF MO calculation gave $S\{(3s)^{1.794}(3p_y)^{0.851}(3p_z)^{1.358}\}$ and $N\{(2s)^{1.861}(2p_y)^{1.319}(2p_z)^{0.845}\}$ populations, which reflect very slight

(1) Each of the structures **5** and **6** has a "long" or formal π-bond (- - -), which links the nonadjacent nitrogen or sulfur atoms. Because the overlap between nonadjacent AO's is very small, such bonds have negligible strengths. Some workers do not indicate the presence of formal bonds, and the VB structures are then referred to as (spin-paired) diradical structures. The relevance of these structures for qualitative VB descriptions of a large number of electron-rich molecules is described in ref 2. See also: Hiberty, P. C.; *Isr. J. Chem.*, **1983**, *23*, 20 and references therein.

(2) Harcourt, R. D. *Lect. Notes Chem.* **1982**, *30*, 1.

(3) Fujimoto, H.; Yokoyama, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 800.

(4) Stewart, R. F. *J. Chem. Phys.* **1970**, *52*, 431.

(5) Wilson, R. M. *J. Chem. Phys.* **1974**, *60*, 1692 and unpublished data. Wilson's "best atom" exponents are similar to those calculated by: Clementi, E.; Raimondi, D. L. *Ibid.* **1963**, *38*, 2686. For S_2N_2, the two sets of exponents give STO-6G VB energies of –901.1822 and –901.1819 au. Because Wilson's "best ion" exponents were readily available, we have also used his "best atom" exponents.

(6) Cohen, M. J.; Gartio, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *J. Am. Chem. Soc.* **1976**, *98*, 3844 and references therein.

(7) (a) Harcourt, R. D.; Roso, W.; *Can. J. Chem.* **1978**, *56*, 1093. (b) *Int. J. Quantum Chem.* **1979**, *16*, 1033. In Table I of ref 7a, the first column of coefficients and the energy, should read as 0.6911, 0.4252, 0.2243, –0.0688, –0.0313, –0.0576, and –216.91 eV.

(8) Chirgwin, B. W.; Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1950**, *201*, 196.

(9) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. The MO calculations allow for greater delocalization of the valence-shell σ-electrons than do our VB calculations. This will contribute to the lowering of the MO energy relative to the VB energy.

Table I. Hybridization Parameters (λ), Energies (E, au), and VB Structure Weights (W_i)

λ_N	λ_S	E	$W_1-W_4{}^c$	W_5	W_6	$W_7-W_8{}^c$	$W_9-W_{10}{}^c$
0.0	0.0	$-901.182\,19^a$	0.271	0.670	0.026	0.026	0.008
0.0	0.0	$-901.196\,30^b$	0.332	0.574	0.047	0.034	0.014
0.2025	0.255	$-901.305\,83^b$	0.351	0.543	0.054	0.036	0.016
0.405	0.510	$-901.249\,07^b$	0.362	0.526	0.058	0.037	0.017
		INDO³	0.372	0.504	0.084	0.020	0.021

^{a} Best atom exponents. ^{b} N, N⁻, S, and S⁺ exponents for valence-shell π-electrons. ^{c} Sum of weights.

Table II. Energies (au) and Weights for Resonance between Eight or Six Lewis Structures^a

| spin (S)	E	W_1-W_4	W_5	W_6	W_7-W_8	W_9-W_{10}
0	$-901.143\,11$	0.847			0.108	0.046
0	$-901.294\,21$	0.359	0.588	0.052		
1	$-901.246\,39$	0.212	0.788	0.0		
0^b	$-900.993\,65$	0.887	0.0	0.0	0.0	0.113

$^a \lambda_N = 0.2025$, $\lambda_S = 0.255$. ^{b} First $S = 0$ excited state.

polarization of the σ-bonds and s–p hybridization. Limitations on computing facilities prevented us from determining the optimum values for λ_S and λ_N by independent variation of these parameters. Approximate estimates were obtained in the following manner. From the above MO populations, we have calculated $\lambda_S = 0.510$ and $\lambda_N = 0.405$. When these values are halved, the VB energy of Table I is close to the minimum obtained when the three VB energies of (b) are plotted against λ_S or λ_N. However, regardless of the nature of the calculation, the spin-paired diradical or "long-bond" structure **5** is calculated to have by far the largest weight—which is in agreement with the result obtained from the INDO study—and is also in accord with the expectations of the electroneutrality principle. Indeed the energy for this structure alone (−901.2038 au) is less than the −901.1431 au calculated for resonance between structures **1–4** and **7–10** (Table II).

In Table II, we have also reported energies and weights for resonance between structures **1–6**, the lowest energy $S = 1$ state (which involves parallel spins for the two electrons that form the π-bond in each of structures **1–6**), and the first $S = 0$ excited state. Structure **5**, which is dominant in the ground state, does not contribute to the first $S = 0$ excited state. In contrast, the $S = 1$ state is calculated to be primarily a (parallel-spin) diradical, with a lower energy than that obtained through resonance between the $S = 0$ structures **1–4** and **7–10**.

S₂N₂ Polymerization and Electron Conduction in (SN)ₓ

Resonance between the $S = 0$ VB structures **1–6** provides an energy which is close to that for the ten-structure calculations. Elsewhere²,¹⁰ it has been shown that this resonance is equivalent to resonance between the "increased-valence" structures **11** and **12**, each of which has two Pauling "3-electron bonds" as components, as is indicated in structures **13** and **14**. Use of **11** ↔
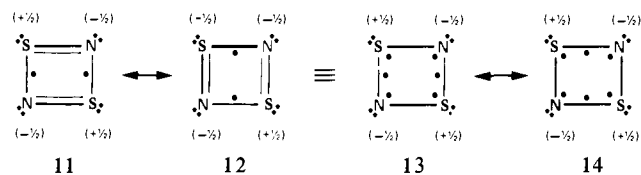

12 therefore provides an economical and low-energy VB representation for the ground state and energetically is to be preferred to resonance between structures **1–4** and **7–10**.

An "increased-valence" representation for the MacDiarmid et al.⁶ mechanism for thermal polymerization of S₂N₂ to (SN)ₓ is that of **15** → **16** → **17**. In **15** we have assumed that due to the
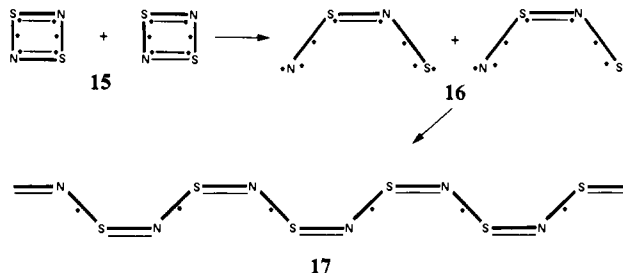
reduction of symmetry when the monomers are juxtapositioned, the S₂N₂ VB structures of type **11** have larger weights than do those of type **12**.

A VB mechanism for electron conduction in (SN)ₓ follows easily from the use of "increased-valence" structure **17** when it is expressed in terms of its Pauling "three-electron bond" components, as in **18**. If it is assumed that the electrons flow from left to right under the influence of an external electric field, we may write
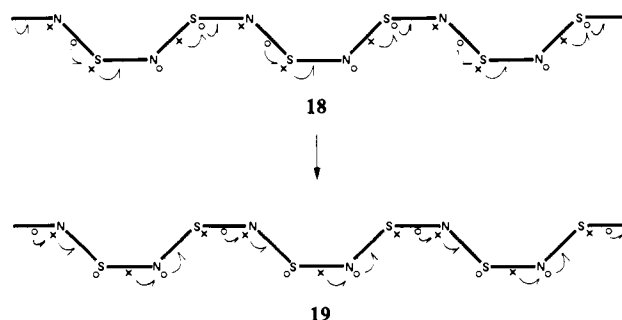
with electrons transferred from S–N bonding MO's into AO's and from AO's into S–N bonding MO's. (In **18** and **19**, the crosses and circles represent electrons with α and β spin wave functions.) This type of VB representation for the conduction depends on the existence of appreciable spin-paired diradical as well as zwitterionic character for (SN)ₓ. We have calculated (Table I) that both of these characteristics are very important for the ground state of the S₂N₂ monomer.

Atomic Orbital Basis Sets

Because we have used a minimal (STO-6G) basis set, our MO energy (−901.36 au) for S₂N₂, although substantially lower than −893.66 au for an STO-3G calculation,¹¹ lies several atomic units above the energies obtained from extended basis set calculations.¹² At present we are unable to utilize an appreciably larger basis set for the VB calculations, and therefore it remains to be demonstrated whether our qualitative conclusions concerning VB weights will alter significantly when an extended basis is used. We note that the results of VB calculations by Hiberty and Ohanessian¹³ for numerous 1,3-dipolar (or zwitterionic diradical hybrid¹⁴) molecules give similar structural weights for minimal (STO-3G) and extended (4-31G) basis sets when a terminal

(10) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5193; **1981**, *103*, 5623. See also ref 2 and Harcourt and Hügel (Harcourt, R. D.; Hügel, H. M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 239) for "increased-valence" descriptions of the bonding for other S–N compounds.

(11) (a) Kertész, M.; Suhai, S.; Ažman, A.; Kocjan, D.; Kiss, Á. I. *Chem. Phys. Lett.* **1976**, *44*, 53. (b) Deutsch, P. W.; Curtiss, L. A. *Ibid.* **1977**, *51*, 125. (c) Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 6687. (d) Millefiori, S.; Millefiori, A.; D'Arrigo, C. *Inorg. Chim. Acta* **1981**, *50*, 167.

(12) The lowest energy reported so far is −904.0244 au with an N-(7,3,1)/S(10,6,1) basis set: Karpfen, A.; Schuster, P.; Petkov, J.; Lischka, H. *J. Chem. Phys.* **1978**, *68*, 3884.

(13) Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1982**, *104*, 66.

oxygen atom is not present. If sulfur 3d orbitals are omitted from the bonding scheme, S_2N_2 may be classified as a 1,3-dipolar (or zwitterionic diradical hybrid) molecule.

Inclusion of sulfur 3d orbitals as hybridization functions would require the inclusion of structures such as **20** and **21**, with an expanded valence shell for one of the sulfur atoms, in the VB basis set. The results of MO calculations[15] indicate that sulfur 3d

20   21
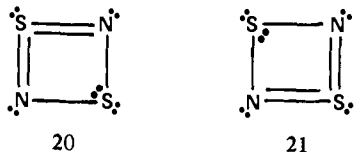
populations are small, and therefore these types of structures will not contribute substantially to the ground-state resonance.

Localized MO's and VB Structures

A number of workers[16h,w,17] have transformed the canonical MO's for S_2N_2 to obtain localized MO's. The resulting VB structures are **20** or **21**[16h,w] and **22**,[17] in which each of the localized MO's is doubly occupied.

22
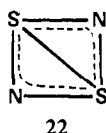
Each of the S–N bonds for **20** or **21** is then calculated to have both σ- and π-character, but in contrast to the discussion for these structures in the previous section, there is no d-orbital involvement as a hybridization function; i.e., the total d-orbital population for each sulfur atom is calculated to be very much less than unity in value. In structure **22**, there are two three-center (S–N–S) π-bonds and an S–S π-bond. The wave functions for structures **20** or **21** with localized MO's and for **22** may always be expressed as linear combinations of the wave functions for the canonical Lewis structures **1–10** (and others), but structures **20–22** do not give any hint that appreciable (singlet) diradical character may be associated with the two nitrogen atoms. In contrast, this diradical character is made evident in the "increased-valence" structures **11** and **12** when they are expressed in terms of their

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(14) Harcourt, R. D. *J. Mol. Struct.* **1972**, *12*, 351. See also ref 2, p 239, ref 7a, and Harcourt and Little (Harcourt, R. D.; Little, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 41).

(15) Our STO-6G MO calculations with neutral atom Slater orbital exponents give energies of −900.2935 and −900.3177 au when sulfur 3d orbitals are excluded and included. For the latter calculation, the total d-orbital population (for $\xi_d = 1/3$) is $0.0525e/S$ atom. Other estimates of total d-orbital populations are as follows: (i) CNDO,[16f,h] 0.1229 (S); (ii) ab initio,[16w] 0.1348 (S), 0.0200 (N). A complete list of MO calculations is provided in ref 16.

(16) EHT: (a) Ref 11a. (b) Salahub, D. R.; Messmer, R. P. *Phys. Rev. B: Solid State* **1976**, *14*, 2592. (c) Burdett, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 5461. (d) Burdett, J. K.; Price, S. L. *Phys. Rev. B: Solid State* **1982**, *25*, 5778. CNDO: (e) Reference 11a. (f) Adkins, R. R.; Dell, R.; Turner, A. G. *J. Mol. Struct.* **1976**, *31*, 403. (g) Salaneck, W. R.; Lin, J. W.-p.; Paton, A.; Duke, C. B.; Caeser, G. P. *Phys. Rev. B: Solid State* **1976**, *13*, 4517. (h) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1383. INDO: (i) Yamabe, T.; Tanaka, K.; Fukui, K.; Kato, H. *J. Phys. Chem.* **1977**, *81*, 727. (j) Millefiori, S.; Millefiori, A. *Inorg. Chim. Acta* **1980**, *45*, L19. MNDO: (k) Brant, P.; Weber, D. C.; Ewing, C. T.; Carter, F. L.; Hashmall, J. A. *Synth. Met.* **1980**, *1*, 161. (l) Brant, P.; Weber, D. C.; Ewing, C. T.; Carter, F. L.; Hashmall, J. A. *Inorg. Chem.* **1980**, *19*, 2829. (m) Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84. Ab initio SCF-Xα: (n) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039. (o) Ref 16b. (p) Batra, I. P.; Ciraci, S.; Rudge, W. E. *Phys. Rev. B: Solid State* **1977**, *15*, 5858. (q) Ching, W. Y.; Harrison, J. G.; Lin, C. C. *Ibid.* **1977**, *15*, 5975. Ab initio SCF±CI: (r) Collins, M. P. S.; Duke, B. J. *J. Chem. Soc., Chem. Commun.* **1976**, 701. (s) Reference 11a. (t) Jafri, J. A.; Newton, M. D.; Pakkanen, T. A.; Whitten, J. L. *J. Chem. Phys.* **1977**, *66*, 5167. (u) Reference 11b. (v) Reference 12. (w) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Egdell, R. G.; Evans, R. *Inorg. Chem.* **1980**, *19*, 1307. (x) Von Niessen, W.; Diercksen, G. H. F. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 95. (y) Reference 11c. (z) Reference 11d. (aa) Palmer, M. H.; Findlay, R. H. *J. Mol. Struct. Theochem.* **1983**, *92*, 373. See also: (bb) Gimarc, B. M.; Trinajstić, N. *Pure Appl. Chem.* **1980**, *52*, 1443. (cc) Náray-Szabá, G. *Ibid.* **1980**, *52*, 1565.

(17) Bhattacharyya, A. A.; Bhattacharyya, A.; Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 7458.

Pauling "three-electron bond" components, as in **13** and **14**.

Elsewhere,[18] it has been deduced that the wave function for the π-electrons of **11** $\leftrightarrow$ **12** (or **13** $\leftrightarrow$ **14**) corresponds to the covalent component of the canonical MO configuration

$$\Psi_1(MO) = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3| \tag{1}$$

$$\propto (1/2)(|\psi_1\bar{\psi}_1\psi_2'\bar{\psi}_2'\psi_3'\bar{\psi}_3'| + |\psi_1\bar{\psi}_1\psi_2''\bar{\psi}_2''\psi_3''\bar{\psi}_3''|) \tag{2}$$

in which

$$\psi_1 = a + c + \kappa(b + d) \qquad \psi_2 = a - c \qquad \psi_3 = b - d \tag{3}$$

are the canonical MO's, a and c are nitrogen AO's, b and d are sulfur AO's, $0 < \kappa < \infty$, and

$$\psi_2' = \psi_2 + \kappa\psi_3 \qquad \psi_3' = \kappa\psi_2 - \psi_3 \qquad \psi_2'' = \kappa\psi_2 + \psi_3$$
$$\psi_3'' = \psi_2 - \kappa\psi_3 \tag{4}$$

are linear combinations of the canonical MO's. This result is obtained[18] by means of unitary transformations of the occupied MO's of eq 2 (cf. ref 19) to give

$$\Psi_1(MO) = -\Psi_{covalent} + \Psi_{ionic} \tag{5}$$

in which $\Psi_{covalent}$ and Ψ_{ionic} respectively represent

$$(N_aS_b)(N_cS_d) + (N_aS_d)(N_cS_b)$$

and

$$(N_aS_b)^+(N_cS_d)^- + (N_aS_b)^-(N_cS_d)^+ + (N_aS_d)^+(N_cS_b)^- + (N_aS_d)^-(N_cS_b)^+$$

distributions for the π-electrons.

When $\Psi_1(MO)$ is linearly combined with doubly-excited configurations that arise from excitations of electrons from the MO's of eq 4 into the canonical MO of eq 6, the importance of $\Psi_{covalent}$

$$\psi_4 = \kappa'(a + c) - (b + d) \tag{6}$$

increases[18] relative to that of Ψ_{ionic}. As has been discussed above, the $\Psi_{covalent}$ corresponds to resonance between the Lewis structures **1–6**. The Ψ_{ionic} is given by eq 7

$$\Psi_{ionic} = |(\psi_{ab})^2(c)^2(d)^2| + |(a)^2(b)^2(\psi_{cd})^2| + |(\psi_{ad})^2(b)^2(c)^2| + |(a)^2(d)^2(\psi_{bc})^2| \tag{7}$$

in which

$$\psi_{ab} = a + \kappa b \qquad \psi_{cd} = c + \kappa d \qquad \psi_{ad} = a + \kappa d$$
$$\psi_{bc} = c + \kappa b \tag{8}$$

and $(\psi_{ab})^2 \equiv \psi_{ab}\bar{\psi}_{ab}$, etc. Inspection of eq 7 shows that Ψ_{ionic} is the wave function for resonance between structures **1–4** when localized MO's rather than Heitler–London wave functions are used to describe the S–N π-bonds of each of these structures. Further, because

$$|...\psi_{ab}\bar{\psi}_{ab}| \equiv |...a\bar{a}| + \kappa^2|...b\bar{b}| + \kappa(|...a\bar{b}| + |...b\bar{a}|)$$

it is easy to deduce that Ψ_{ionic} is a wave function for resonance between VB structures **1–4** (with Heitler–London wave functions for the π-bonds) and **7–10**. The "best" wave function for this resonance (Table II) is calculated to lie considerably above that of $\Psi_{covalent}$ for resonance between structures **1–6**. Thus, according to these MO-CI considerations, resonance between "increased-valence" structures must provide the primary ground-state VB description for the π-electrons of S_2N_2.

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(18) Harcourt, R. D., to be submitted for publication. The $\psi_{covalent}$ of eq 5 involves one variation parameter, κ. The "best" $\psi_{covalent}$ must involve two variation parameters. See footnote 9 of ref 10 for the procedure that may be used to construct this type of "increased-valence" wave function.

(19) Examples of such unitary transformations for extended six-electron four-center bonding units are provided in ref 2, p 109. (a) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195; **1981**, *103*, 5623. (b) Harcourt, R. D. *Aust. J. Chem.* **1979**, *32*, 933.