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Valence Bond Structures for the D_{2h} Isomer of N_2O_4 and Some Isomers of S_3O_2 and S_3O

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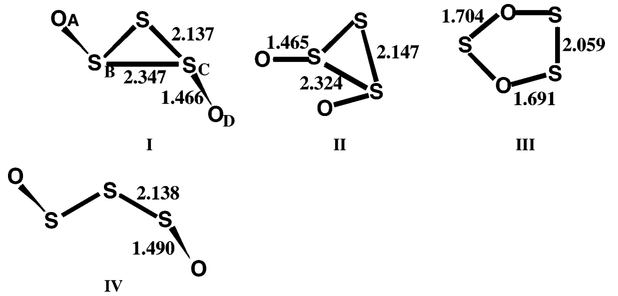
The construction of valence bond structures of the increased-valence type is re-described for the D_{2h} isomer of N_2O_4 and applied to obtain the corresponding valence bond structures for isomers of S_3O_2 and S_3O, each of which has at least one six-electron four-center bonding unit. It is discussed how the S–O and S–S bond properties that are associated with the S_3O_2 and S_3O increased-valence structures are in qualitative accord with the calculated bond lengths. The qualitative six-electron four-center molecular orbital theory for the symmetrical O–S–S–O component of each S_3O_2 isomer is related to the increased-valence structure for the six electrons. An increased-valence structure for the lowest-energy S_3O_2 isomer is equivalent to a restricted form of resonance between 16 Lewis-type valence bond structures. The two types of S–S bond length are used to provide empirical estimates of the weights for these Lewis structures and are compared with those obtained from the results of STO-6G valence bond calculations for the $^3\Sigma^-$ ground state of SO.

1. Introduction

The two lowest-energy isomers of S_3O_2, **I** and **II** here and **1** and **2** in ref 1, have been calculated by Wong and Steudel[1] to have C_2 and C_s symmetries, respectively. The energy separation is 4 kJ mol^{-1}, with the C_2 isomer having the lower energy. Thirteen other isomers have substantially higher energies.[1] The lengths for the S−O and S−S bonds are respectively similar to the 1.48 Å length for the double bond[2] of free $^3\Sigma^-$ SO and longer than the 2.06 Å length for a S−S single bond,[3] as in HSSH. The S_B-S_C bond for each isomer is longer than the S_B-S and S_C-S bonds. For the cyclic C_2 isomer **10** of ref 1 or **III** here, the S−O bond lengths of 1.704 and 1.691 Å and the S−S length of 2.059 Å are essentially those for S−O and S−S single bonds.

Scheme 1



In Scheme 1 of ref 1, as a minor component of ref 1, six Lewis-type valence bond (VB) structures are displayed for isomers **I** and **II**. Resonance between these structures was used to account qualitatively for the calculated bond lengths of these isomers. In the present paper, VB procedures described previously[4−13] for the D_{2h} isomer of N_2O_4 (and also for (a)[7,14,15] SO, SO_2, S_2O and S_2O_2 and (b)[16] S_2O_3) will be used to provide an alternative VB approach to the bonding for isomers **I** and **II**, via the construction of VB structures that are designated as increased-valence structures.[4−16] The

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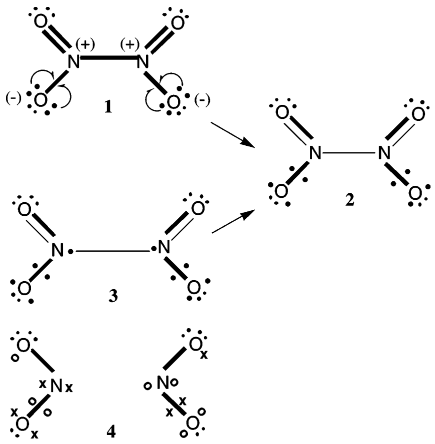

Figure 1. Valence-bond structures for N_2O_4 and NO_2 components. Each of **1**−**3** participates in resonance with three other VB structures, which differ in the locations of the electrons in the N−O bonds.

distribution of the six active-space electrons in the symmetrical $O_A-S_B-S_C-O_D$ component of the primary VB structure for S_3O_2 will also be related to a qualitative molecular orbital (MO) approach[17] to six-electron four-center bonding. The construction and properties of increased-valence structures for some open chain S_3O isomers, with either one or two nonsymmetrical six-electron four-center bonding, will then be discussed. The purpose is to provide illustrative examples of how classical VB concepts can be used to obtain easily qualitative insights into the origins of bond properties. In contrast to the approach used in the "modern" VB theory of ref 18, classical VB concepts do not accommodate electrons in multicenter orbitals.

Increased-valence structures, for example, the N_2O_4, S_3O_2, and S_3O VB structures of type **2** in Figures 1, 2, and 4, are equivalent to resonance between Lewis-type VB structures.[4−15] Empirical estimates of the weights for the latter structures for the lowest-energy S_3O_2 isomer are determined from the S−S bond lengths.

2. Lewis and Increased-Valence Structures for N_2O_4 and S_3O_2

Familiar types of classical VB structures for diamagnetic molecules usually involve two-center electron-pair bonds between pairs of adjacent atoms and lone pairs of electrons.

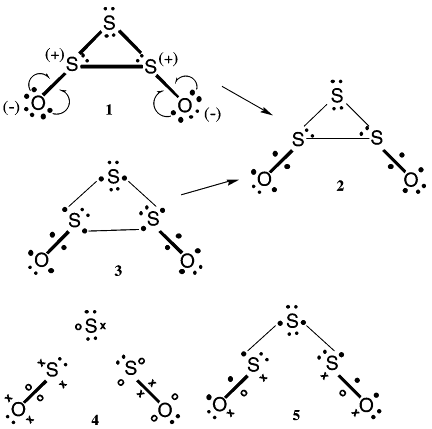

Figure 2. Valence-bond structures for S_3O_2. (As in ref 1, the structures are drawn with C_{2v} symmetry.)

The Lewis octet VB structures **1** in each of Figures 1, 2, and 4 and the Lewis structures **a** and **c**−**f** of scheme 1 of ref 1 (also cf. ref 19) are examples. Less-widely used classical VB concepts for diamagnetic (as well as paramagnetic) molecules include one-electron bonds, (Pauling) diatomic three-electron bonds (or three-electron two-orbital bonds or three-electron half-bonds, which are essentially one-electron bonds, see Appendix 1), and singlet-diradical (or "long-bond", or "formal bond", or Dewar-type) Lewis structures. The Lewis structure **b** of ref 1 is an example of a singlet-diradical structure. As previously discussed on many occasions[4−16,20−22] and as will be demonstrated again below, VB structures of type **2** in Figures 1, 2, and 4 include three-electron two-orbital bonds as diatomic components and are equivalent to resonance between both types of Lewis structures. These "composite" VB structures of type **2**, with three-electron two-orbital bonds as well as ("normal" and "fractional") electron-pair bonds, are examples of "increased-valence" structures,[4−16,20−22] some properties for which will now be discussed.

The standard octet Lewis structure **1** in each of Figures 1 and 2 possesses adjacent positive formal charges on the nitrogen or sulfur atoms of the N−N or S_B-S_C bond and negative formal charges on two oxygen atoms. The magnitudes of these formal charges can be reduced via one-electron delocalizations[25] from the negatively charged oxygen atoms into N−O or S−O bonding MOs, as indicated in VB structure **1** of Figures 1 and 2. The resulting VB structure **2** involves an *apparent* violation of the Lewis−Langmuir octet rule for the nitrogen or the S_B and S_C atoms; i.e., 10 rather than 8 electrons *appear* to be involved in bonding to each of these atoms. This property, together with the increased-

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(18) See, for example: Gerratt, J.; Cooper, D. L.; Karadakov, P. B.; Raimondi, M. *Chem. Soc. Rev.* **1997**, *26*, 87.

(19) Either one or two S=O double bonds are present in each of the VB structures **a**−**d** of ref 1, and an expansion of the valence shell is associated with the sulfur atom. No valence shell expansion occurs for the sulfur atom of either the $S^{(+)}$=O double bond in each of the structures **e** and **f** of ref 1 or the S÷O double bonds of increased-valence structure **2** of Figure 2.

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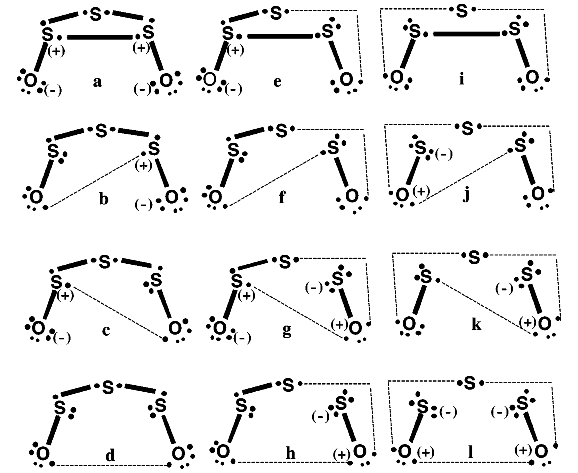

Figure 3. Component Lewis structures[27] for the S_3O_2 increased-valence structure **2** of Figure 2. Mirror-image structures for **e**−**h** are not displayed. (When two-center Coulson−Fischer-type MOs[28] rather than one-center AOs are used to formulate the Heitler−London type wavefunctions for the (fractional) electron-pair bonds of increased-valence structures, additional Lewis-type VB structures are introduced into the resonance scheme; cf., for example, eqs 8−13 of ref 15). For clarity, non-active space sulfur lone-pair electrons are not shown.

valence designation for VB structure **2**, has its origin[4−16,20−22] in the inclusion of singlet-diradical Lewis structures as well as the standard Lewis structures in the component Lewis structure resonance scheme.

Two (fractional) electron-pair N−O π-bonds and a (fractional) electron-pair N−N σ bond are present in increased-valence structure **2** for N_2O_4 in Figure 1. (Fractional electron-pair bonds are symbolized by the use of thin bond lines (—) in increased-valence structures.[4−16,20−22]) With Heitler−London atomic orbital (AO) formulations of the wavefunctions for the fractional electron-pair bonds, this VB structure is equivalent to resonance between Lewis structure **1** and 15 singlet-diradical Lewis structures.[7,8] Therefore, increased-valence structure **2** is more stable than the Lewis structure **1** alone. Twelve of the corresponding sixteen Lewis structures for S_3O_2 are displayed in Figure 3. Each set of 16 Lewis structures is obtained by application of the three-electron two-orbital bond identity (see Appendix 1)

$$\dot{\mathbf{A}}\bullet\dot{\mathbf{B}} = \ddot{\mathbf{A}}\quad\dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{A}}\quad\ddot{\mathbf{B}}$$

to each of the one-electron S−O or N−O bonds in VB structure **2**. If the odd electron has an $m_s = +{}^1/_2$ spin quantum number, then the identity (see Appendix 1) is

$$\overset{\times}{\mathbf{A}}\circ\overset{\times}{\mathbf{B}} = \overset{\times\circ}{\mathbf{A}}\quad\overset{\times}{\mathbf{B}} \leftrightarrow \overset{\times}{\mathbf{A}}\quad\overset{\circ\times}{\mathbf{B}}$$

in which, following Green and Linnett,[23] crosses and circles (x and o) represent electrons with $m_s = +{}^1/_2$ and $m_s = -{}^1/_2$ spin quantum numbers, respectively.

The absence of S−S σ bonds in some of the Lewis structures of Figure 3 is in accord with the presence of long S−S bonds in isomers **I** and **II** relative to the length of 2.06 Å for a normal S−S single bond. Lengthening of the S_B−S_C bond is also associated with (a) the nonbonded repulsions due to the presence of doubly occupied sulfur AOs on the S_B and S_C atoms in Lewis structures **d**, **h**, and **l** of Figure 3 and (b) the orientations of the sulfur AOs (cf. refs 10 and 26).

Because of the absence of S−S σ-bonds in many of the Lewis structures of Figure 3, these bonds are fractional in increased-valence structure **2** of Figure 2.

In Figure 1, increased-valence structure **2** for N_2O_4 is also constructed by spin-pairing the delocalized odd-electron of each NO_2 monomer whose increased-valence structures are those of **3** and their mirror images.[4b,6−10,12,13,22,26] Similarly, singlet ($S = 0$) spin-pairing of the unpaired electrons of two-triplet-spin ($S = 1$) SO monomers with those of a sulfur atom, as shown in structure **3** of Figure 2, generates the increased-valence structure **2** of Figure 2 for S_3O_2. As a consequence, the S−O bond lengths for the S_3O_2 isomers **I** and **II** are similar to those for the SO monomer, as are the lengths of the S−O bonds of the triplet-spin isomer **4** of ref 1 or **IV** here, with increased-valence structure **5** of Figure 2, for which $S = M_S = +1$.

3. Molecular Orbital Theory for Six-Electron Four-Center Bonding

We now relate aspects of the VB theory of Section 2 to the MO theory for six-electron four-center bonding. (Initially, the wavefunction for the N−N or S_B−S_C σ bond in the VB structure **1** in Figures 1 and 2 is formulated as a doubly occupied MO rather than via the Heitler−London AO procedure.)

The MO rationalization[17] for the lengthening of the N−N bond of N_2O_4 involves some delocalization of oxygen lone-pair electrons into the antibonding N−N σ^* MO, which is vacant in VB structure **1** of Figure 1. Similarly, some delocalization of oxygen lone-pair electrons into the vacant antibonding S−S σ^* MO in VB structure **1** of Figure 2 provides the analogous MO explanation for the lengthening of the S_B−S_C bonds of the S_3O_2 isomers **I** and **II**. The associated (local C_{2v}) symmetry a_1 and b_2 MOs are those of eqs 1 and 2, respectively.

$$\psi_1 = a + d + \lambda(b + c),\ \psi_3 = \lambda^*(a + d) - (b + c) \quad (1)$$

$$\psi_2 = a - d + k(b - c),\ \psi_4 = k^*(a - d) - (b - c) \quad (2)$$

In these MOs, a and d are the oxygen AOs that overlap with the sulfur AOs b and c of the S_B−S_C σ bond, λ and k are mixing parameters, with λ^* and k^* chosen so that ψ_1 is orthogonal to ψ_3 and ψ_2 is orthogonal to ψ_4. Because MO ψ_4 is nearest-neighbor O_A−S_B, S_C−O_D, and S_B−S_C antibon-

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(23) Green, M.; Linnett, J. W. *J. Chem. Soc.* **1960**, 4959. See also: Linnett, J. W. *Sci. Prog. (Oxford, U.K.)* **1972**, *60*, 1.

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(25) Each SS(SO) moiety of **2**, with two fractional S−SO bonds, is analogous to an increased-valence structure for F_2SO, with two fractional F−SO bonds (cf. refs 7, 14, and 22a,b). For the S_3O_2 isomers **I** and **II**, the (local) 2pπ and 2pπ'AOs on O_A overlap primarily with the S_B−S and S_B−S_C orbitals. Similarly, the (local) 2pπ and 2pπ'AOs on O_D overlap primarily with the S_C−S and S_C−S_B orbitals. In eqs 1−6, the a and d AOs are the 2pπ' AOs centered on O_A and O_D.

ding, this MO has the highest energy, and therefore it is vacant in the lowest-energy MO configuration, $\Psi_1(\mathrm{MO})$ of eq 3.

$$\Psi_1(\mathrm{MO}) = |\psi_1^{\alpha}\psi_1^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_3^{\alpha}\psi_3^{\beta}| \qquad (3)$$

With $\psi_{ab} = a + kb$, $\psi_{\mathrm{dc}} = d + kc$ as A−B and D−C bonding MOs, and $\psi^*_{ab} = k^*a - b$, $\psi^*_{dc} = k^*d - c$ as A−B and D−C antibonding MOs, on several occasions[6,7,13] it has been deduced that $\Psi_1(\mathrm{MO})$ can be transformed and expressed according to eq 4.

$$\begin{aligned}\Psi_1(\mathrm{MO}) \propto\ & |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{dc}^{\alpha}\psi_{dc}^{\beta}\psi^{*\alpha}_{ab}\psi^{*\beta}_{dc}| + \\ & |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{dc}^{\alpha}\psi_{dc}^{\beta}\psi^{*\alpha}_{dc}\psi^{*\beta}_{ab}| + \\ & |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{dc}^{\alpha}\psi_{dc}^{\beta}\psi^{*\alpha}_{ab}\psi^{*\beta}_{ab}| + \\ & |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{dc}^{\alpha}\psi_{dc}^{\beta}\psi^{*\alpha}_{dc}\psi^{*\beta}_{dc}| \qquad (4)\end{aligned}$$

$$\equiv \Psi(\mathrm{covalent}) + \Psi(\mathrm{ionic}) \qquad (5)$$

The primary ionic structures for S_3O_2 are of the types $(OS)^-S(SO)^+$ and $(OS)^+S(SO)^-$, which arise from $\psi^*_{dc} \rightarrow \psi^*_{ab}$ and $\psi^*_{ab} \rightarrow \psi^*_{dc}$ electron transfers from the covalent (OS)S(SO) structure. Whereas SO has four bonding electrons, the $(SO)^-$ and $(SO)^+$ species have three and five bonding electrons, respectively. The corresponding transformations for 10-electron 6-center bonding are provided in refs 4b and 5b.

As done in refs 6, 7, and 13, the application of the generalized three-electron two-orbital bond identities (cf. Appendix 1) of the type $|\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi^{*\alpha}_{ab}| \propto |a^{\alpha}\psi_{ab}^{\beta}b^{\alpha}|$ to the $\Psi(\mathrm{covalent})$ of eq 4 gives eq 6

$$\begin{aligned}\Psi(\mathrm{covalent}) \propto\ & |a^{\alpha}\psi_{ab}^{\beta}b^{\alpha}d^{\beta}\psi_{dc}^{\alpha}c^{\beta}| + \\ & |d^{\alpha}\psi_{dc}^{\beta}c^{\alpha}a^{\beta}\psi_{ab}^{\alpha}b^{\beta}| \qquad (6)\end{aligned}$$

for $\Psi(\mathrm{covalent})$, which is the wavefunction for the six-electron four-center bonding unit for the $O_A{-}S_B{-}S_C{-}O_D$ of the increased-valence structure **2** in Figure 2. As deduced in refs 6, 7, and 13, MO configuration interaction, primarily via the interaction of $\Psi_1(\mathrm{MO})$ with $\Psi_2(\mathrm{MO}) = |\psi_1^{\alpha}\psi_1^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}|$, increases the importance of $\Psi(\mathrm{covalent})$ relative to $\Psi(\mathrm{ionic})$. Therefore, the VB structure **2** provides the primary VB representation for the six active-space electrons of $O_A{-}S_B{-}S_C{-}O_D$.

Inspection of eq 4 shows that the (fractional) $S_B{-}S_C$ bonding arises from the singlet-spin-pairing of the two electrons that occupy the antibonding $O_A{-}S_B$ and $S_C{-}O_D$ MOs $\psi^*_{ab} = k^*a - b$ and $\psi^*_{dc} = k^*d - c$. In agreement with figure 3 of ref 1, the highest-occupied MO $\psi_3 = \lambda^*a - b - c + \lambda^*d$ of eq 1 in the lowest-energy MO configuration $\Psi_1(\mathrm{MO})$ is $O_A{-}S_B$ and $S_C{-}O_D$ antibonding and $S_B{-}S_C$ bonding.

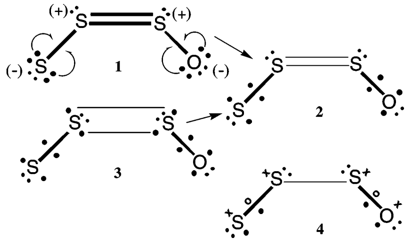

Figure 4. VB structures for S_3O.

4. Increased-Valence Structures for S_3O

The structures for nine isomers of S_3O have also been calculated.[29] There are four open-chain isomers, as $S_A{-}S_B{-}S_C{-}O$. Two of them (isomers **1b** and **1c** of ref 29) have singlet spin states and two (isomers **1f** and **1g** of ref 29) have triplet spin states. Each isomer has an $S_C{-}O$ bond length that is similar to the 1.48 Å length for SO. The $S_A{-}S_B$ bond lengths of 1.94−1.97 Å are shorter than the 2.06 Å for an S−S single bond but longer than the 1.89 Å for the double bond[2] of S_2. The electronic structures of the $S_A{-}S_B$ and $S_C{-}O$ bonds in the singlet-spin and triplet-spin increased-valence structures **2** and **3** of Figure 4 are in accord with the calculated $S_A{-}S_B$ and $S_C{-}O$ bond lengths.

The $S_B{=}S_C$ double bond of VB structure **2** of Figure 4 with two fractional electron-pair bonds is a fractional double bond. The calculated $S_B{-}S_C$ bond lengths of 2.055 and 2.054 Å for the singlet-spin isomers **1b** and **1c** of ref 29 are substantially longer than the 1.89 Å length for the double bond of S_2. Therefore, the presence of a fractional S=S bond in VB structure **2** is in accord with the $S_B{-}S_C$ bond lengths calculated for **1b** and **1c**. Similar types of VB structure/bond-length considerations have been provided[7,10] for the C_{2v} isomers of S_2O_2 and S_4 (cf. refs 30−32 for experimental or calculated estimates of the bond lengths).

Two nonsymmetrical six-electron four-center bonding units—one for σ electrons and one for π electrons—are present in the singlet-spin increased-valence structure **2** of Figure 4. (Increased-valence and MO theory for nonsymmetrical six-electron four-center bonding units is described in ref 33.) For the triplet-spin increased-valence structure **4** of Figure 4, two three-electron two-center bonding units replace the six-electron four-center bonding unit for the π electrons. Therefore, there is no $S_B{-}S_C$ π bonding in this

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(26) (a) Harcourt R. D.; Wolynec, P. P. *J. Phys. Chem. A* **2000**, *104*, 2138, 2144. (b) Harcourt R. D.; Wolynec, P. P. *J. Phys. Chem. A* **2001**, *105*, 4974.

(27) Because there are six singly occupied orbitals (two antibonding $O_A{-}S_B$ MOs, two antibonding $S_C{-}O_D$ MOs, and two primarily 3p AOs on the central sulfur atom S), there are five Rumer-type singlet-spin-pairing schemes. The primary (lowest-energy) spin-pairing scheme that is needed to obtain increased-valence structure **2** from the triplet-spin VB structures for the two SO involves a linear combination of eight $M_S = 0$ spin Slater determinants. The electron spins that are associated with one of the Slater determinants are shown in structure **4** of Figure 2, also, cf. structure **4** of Figure 1 for N_2O_4. It is noted that inclusion of the other four Rumer spin-pairing schemes, in each of which there is less nearest-neighbor bonding than there is in Figure 3, introduces an additional 64 (less-important) structures into the equivalent Lewis-structure resonance scheme.

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(30) Lovas, F. J.; Tiemann, E.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5005.

(31) Wong, M. W.; Steudel, R., *Chem. Phys. Lett.* **2003**,*379*, 162.

(32) Gottlieb, C. A.; Thorwirth, S.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2005**, *619*, 939. The (C_{2v} symmetry) S=S−S=S VB structure displayed in this reference is for S_4^{2+}, not for S_4.

(33) Harcourt, R. D.; Klapötke, T. M.; White, P. S. *Inorg. Chem. Acta* **1998**, *269*, 1.

Table 1. Empirical Estimates of the Weights for the Lewis Structures of Figure 3[a]

	a	
1.6 1.4 (1.6)	1.6 1.4 (1.6)	1.6 1.4 (1.6)
a = 0.53, 0.48 (0.03)	**e** = **e′** = 0.06, 0.07 (0.04)	**i** = 0.01, 0.01 (0.06)
b = 0.12, 0.13 (0.04)	**f** = **f′** = 0.01, 0.02 (0.06)	**j** = 0.00, 0.00 (0.08)
c = 0.12, 0.13 (0.04)	**g** = **g′** = 0.01, 0.02 (0.06)	**k** = 0.00, 0.00 (0.08)
d = 0.03, 0.02 (0.06)	**h** = **h′**= 0.00, 0.00 (0.08)	**l** = 0.00, 0.00 (0.12)

[a] Structures **e′**−**h′**, the mirror images of **e**−**h**, are not displayed in Figure 3. For weights in parentheses, see text.

increased-valence structure. The calculated lengths of 2.236 and 2.334 Å for the $S_B{-}S_C$ bond in the triplet-spin isomers **1f** and **1g** of ref 29 are in accord with the absence of $S_B{-}S_C$ π bonding in VB structure **4**, which involves only a fractional $S_B{-}S_C$ σ bond. Electron-spin correlation between the singly occupied antibonding $S_A{-}S_B$ and $S_C{-}O$ π-electron MOs (with parallel spins) in this VB structure must also make some contribution to the $S_B{-}S_C$ bond lengthening of isomers **1f** and **1g** of ref 29 relative to the lengths of this bond in isomers **1b** and **1c** of ref 29.

In refs 4b, 6, 7, and 34, VB structures that are analogous to those for S_2O_2 are displayed for N═N bonded dimers of RNO.

5. Estimates of Weights for the Lewis VB Structures of Figure 3

Pauling's bond-number, the (n) bond-length ($r(n)$) formula[35] of eq 7

$$r(n) = 2.06 - a \log n \qquad (7)$$

will now be used to obtain empirical estimates of the bond numbers for the S−S bonds of the S_3O_2 isomer **1** of ref 1, i.e., **I** here. From these bond numbers, empirical estimates of the weights for the Lewis structures of Figure 3 will then be deduced.

The value for the constant a in eq 7 can be determined from an estimate of ~3.0 Å[32] for the two intermoiety S−S bond lengths for $S_6N_4^{2+}$ dimers of $S_3N_2^+$. As discussed in refs 7, 13, and 36, the four sulfur atoms that participate in the intermoiety bonding involve a cyclic six-electron four-center bonding unit. For large distances between the $S_3N_2^+$ moieties, the primary responsibility for the AO overlap contribution to this bonding arises from the (singlet) spin-pairing in a σ manner of the π^*(SS) electron of one $S_3N_2^+$ moiety with the π^*(SS) electron of the other $S_3N_2^+$ moiety. (The results of STO-6G calculations (see Appendix 2) provide support for this conclusion.) This spin-pairing generates an intermoiety S−S bond order of 0.25[4a,7,37,38] to give a value of 1.6 for a.

Using eq 7 with a = 1.6, lengths of 2.347 and 2.137 Å for the $S_B{-}S_C$ and $S_B{-}S$ ($\equiv S{-}S_C$) bonds give $n(S_B{-}S_C) = 0.662$ and $n(S_B{-}S) = n(S{-}S_C) = 0.895$. In refs 4a, 5b, 6, and 7, it is deduced that the bond numbers are equivalent to the products of the odd-electron charges (c^2 here) for the electrons that occupy the AOs, which overlap to form the (fractional) bonds. Thus, $n(S_B{-}S_C) = c_x^2(S_B){\cdot}c_x^2(S_C)$ with $c_x^2(S_B) \equiv c_x^2(S_C)$, $n(S_B{-}S) \equiv n(S{-}S_C) = c_y^2(S_B){\cdot}c'^2(S) \equiv c''^2(S){\cdot}c_y^2(S_C)$ with $c_y^2(S_B) \equiv c_y^2(S_C)$, and $c'^2(S) \equiv c''^2(S) = 1$. The resulting values for the odd-electron charges $c_x^2(S_B) \equiv c_x^2(S_C)$ and $c_y^2(S_B) \equiv c_y^2(S_C)$ are 0.81363 and 0.895, respectively, to give $c_x^2(O_A) \equiv c_x^2(O_D) = 0.18637$ and $c_y^2(O_A) \equiv c_y^2(O_D) = 0.105$.

For the S_3O_2 isomer **I**, we shall now assume that:

(a) The (valence-shell) antibonding π_x^*(SO) electrons of two SO monomers are spin-paired to form fractional $O_A{-}S_C$, $O_A{-}O_D$, $S_B{-}S_C$, and $S_B{-}O_D$ σ bonds. For a given distribution of the remaining electrons of S_3O_2, the resulting weights for the Lewis-type VB structures with these types of bonds are $c_x^2(O_A){\cdot}c_x^2(S_C) \equiv c_x^2(S_B){\cdot}c_x^2(O_D) = 0.151636$, $c_x^2(O_A){\cdot}c_x^2(O_D) = 0.034733$, and $c_x^2(S_B){\cdot}c_x^2(S_C) = 0.662$.

(b) The (valence-shell) antibonding π_y^*(SO) electron of an SO monomer is spin-paired with one of the odd electrons of the bridging sulfur atom of S_3O_2 to form fractional $O_A{-}S$, $S_B{-}S$, $S{-}S_C$, and $S{-}O_D$ σ bonds. For a given distribution of the remaining electrons of S_3O_2, the resulting weights for the Lewis-type VB structures with these types of bonds are $c_y^2(O_A){\cdot}c'^2(S) \equiv c''^2(S){\cdot}c_y^2(O_D) = 0.105$ and $c_y^2(S_B){\cdot}c'^2(S) \equiv c''^2(S){\cdot}c_y^2(S_C) = 0.895$.

When the weights for the two sets of Lewis structures are combined, we obtain the (non-parentheses) weights of Table 1 for the Lewis structures of Figure 3.

We have repeated the calculations of the weights, using a = 1.4, which is obtained from a calculated length[39] of 2.89 Å for the long S−S bonds of the high-energy rectangular $(S_2^+)_2$ isomer of S_4^{2+}.

The results of STO-6G VB calculations with best-atom exponents (cf. Appendix 3) for the $^3\Sigma^-$ ground state of SO give $c_x^2(S) \equiv c_y^2(S) = 0.4153$ and $c_x^2(O) \equiv c_y^2(O) = 0.5847$. If it is assumed that these quantities do not change when the spin-pairings of points (a) and (b) above occur, the weights reported in parentheses in Table 1 are obtained. The weights deduced from the bond lengths imply that, as would be expected, the distributions of the odd electrons (and hybridization) of the sulfur AOs for each SO monomer change substantially when the S_3O_2 isomer **I** is formed. Obviously, better basis sets could generate somewhat different estimates for $c_x^2(S) = c_y^2(S)$ in the SO monomer, but

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(34) Harcourt, R. D.; Skrezenek, F. L.; Gowenlock, B. G. *J. Mol. Struct. THEOCHEM* **1993**, *284*, 87.

(35) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 255.

(36) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784 and references 11, 12b, and 14 therein.

(37) Harcourt, R. D. *J. Phys. Chem.* **1993**, *97*, 1351. In this reference, an alternative type of increased-valence structure to that of structure **2** of Figure 1 is also presented.

(38) Brownridge, S.; Crawford, M-J.; Du. H; Harcourt, R. D.; Knapp, C.; Laitinen, R. S.; Passmore, J.; Rautiainen, J. M.; Suontamo, R. J.; Valkonen, J. *Inorg. Chem.* **2007**, *46*, 681 and Section 6 of the Supporting Information, (in which the designation bond-order is used).

(39) Krossing, I; Passmore, J. *Inorg. Chem.* **1999**, *38*, 5203. The calculated value of 0.283 for the bond order of each of the intermolecular S−S bonds of rectangular $(S_2^+)_2$ is similar to the S−S bond-number of 0.25 that has been used to determine the value of a in eq 7. The two-electron bond number rather than the bond order is the appropriate bond index to determine the weights for the Lewis structures of Figure 3.

the weights obtained from the bond lengths show that $c_x^2(\mathrm{S_B}) \neq c_y^2(\mathrm{S_B})$ and $c_x^2(\mathrm{S_C}) \neq c_y^2(\mathrm{S_C})$ for isomer **I**.

6. Conclusions

The interrelations that exist between the primary features of the electronic structures of N_2O_4, two S_3O_2 isomers, and S_3O have been demonstrated by the use of increased-valence structures. With regard to these types of VB structures, a referee for ref 40 has written: "Increased-valence structures can illustrate the electronic structures of molecules concisely and intuitively as each increased-valence structure can be decomposed into a number of conventional Lewis structures". The VB structures displayed in Figures 2 and 3 for S_3O_2 provide an illustration of this statement.

It is sometimes said that "a picture is worth one thousand words", and the increased-valence structures displayed in Figures 2 and 4 show immediately that the lengths of (a) the S−O and S−S bonds of three S_3O_2 isomers are respectively similar to those of S−O double bonds but longer than S−S single bonds and (b) the S−O bond and one S−S bond for an S_3O isomer are similar to those of an S−O or S−S double bond, whereas the other S−S bond of this isomer is longer than an S−S double bond. No calculations are needed to obtain some qualitative insight into the nature of the primary features of the electronic structures of the molecules considered in this paper.

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Appendixes

1. Orbital configurations for the three-electron two-orbital identity are $(a)^1(\psi_{ab})^1(b)^1 = (a)^2(b)^1 + k(a)^1(b)$,[2] with the spin of the ψ_{ab} electron opposed to the parallel spins of the a and b electrons in $(a)^1(\psi_{ab})^1(b)$.[1] Also, $(a)^1(\psi_{ab})^1(b)^1$ is proportional[23] to $(\psi_{ab})^2(\psi^*_{ab})$,[1] in which a and b are overlapping AOs, k is a polarity parameter (>0 when $<a|b> > 0$), and $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$ are orthogonal bonding and antibonding MOs. $|a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}|$ and $|a^{\beta}\psi_{ab}{}^{\alpha}b^{\beta}|$ are the Slater determinants for $(a)^1(\psi_{ab})^1(b)^1$ when the odd electron has $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ spin quantum numbers, respectively. See also ref 24 for further development of theory for the three-electron two-orbital bond.

2. For $(S_2{}^+)_2$, Roso's ab initio VB program[41] and AO exponents for $\frac{1}{2}(S + S^+)$[42a] have been applied to the all-electron STO-6G VB calculations for $(S_2{}^+)_2$ with S−S bond lengths of (a) 2.1 and 3.0 Å and (b) 1.82 and 2.89 Å. With ψ^*_{ab} and ψ^*_{cd} as the singly occupied (in-plane) antibonding π^*_y MOs of the $S_2{}^+$ monomers, which overlap to form the fractional intermolecular S−S σ bonds, the following wavefunctions, with normalized configurations, have been constructed: (a) $\Psi(S_2{}^+)_2 = (\psi^*_{ab})^1(\psi^*_{cd})^1 + 0.283\{(\psi^*_{ab})^2 + (\psi^*_{cd})^2\}$ and (b) $\Psi(S_2{}^+)_2 = (\psi^*_{ab})^1(\psi^*_{cd})^1 + 0.383\{(\psi^*_{ab})^2 + (\psi^*_{cd})^2\}$. (The remaining 20 valence-shell electrons were located in 3s AOs, diatomic bonding MOs of the in-plane π_y (ψ_{ab} and ψ_{cd}) and σ_z types, and out-of-plane π_x type. All inner-shell electrons doubly occupy the twenty 1s, 2s, and 2p AOs.) Similar types of VB calculations for $\Psi(S_2{}^+)_2 = (\psi^*_{ab})^1(\psi^*_{cd})^1 + \lambda(\psi^*_{ad})^1(\psi^*_{bc})^1$ give (a) $\lambda = 0.685$ and (b) $\lambda = 0.502$; i.e., $(\psi^*_{ab})^1(\psi^*_{cd})^1$ is the primary spin-pairing process.

The intermolecular C−C bonding for tetracyanoethenide dimers[43] ($[\mathrm{TCNE}]_2{}^{2-}$) can be similarly described.

3. With $r(\mathrm{SO}) = 1.48$ Å, best-atom AO exponents[44] and 12 $S = 1$ spin Lewis structures that differ in the distributions of two $2p\sigma(\mathrm{O})$ and $3p\sigma(\mathrm{S})$ electrons, three $2p\pi_x(\mathrm{O})$ and $3p\pi_x(\mathrm{S})$ electrons, and three $2p\pi_y(\mathrm{O})$ and $3p\pi_y(\mathrm{S})$ electrons, Roso's ab initio VB[38] program has been used to perform the STO-6G VB calculations for the ground state of the SO monomer.

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