J. Phys. Chem. A **2009,** *113,* 8677–8682

Characterization of the Weak SS Bonds in the OSSSO and O_2SSSO_2 Molecules

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Received: April 3, 2009; Revised Manuscript Received: May 18, 2009

The weak S1−S3 bonds in the OSSSO *trans*-disulfoxide and the corresponding sulfone, O_2SSSO_2, are readdressed at the B3LYP/6-31+G(d) level using both the atoms-in-molecules (AIM) and the electron localization function (ELF) approaches. The S1−S3 bonds are clearly characterized as fractional (i.e., with a bond number or bond order which is less than unity) or protocovalent and are very similar in nature to the weak N−N bond in O_2NNO_2. These results are in accord with what is obtained by inspection of valence bond structures of the increased-valence type.

Introduction

Wong and Steudel[1] have carried out high-level theoretical calculations on some 15 isomers of S_3O_2, experimentally unknown species. They found that the oxygen atoms prefer terminal and exocyclic positions, with the 1−3-*trans*-disulfoxide being the most stable species, followed closely by the cis analogue (about 4.0 kJ mol^{-1} higher in energy). Their extensive calculations provide benchmark results for the molecular geometries and relative energies of these systems. Labeling the sulfur atoms as S1, S2, and S3, with the oxygen substitution at the 1 and 3 positions, a weak S1−S3 bond was found, whose bond order (as measured by the electron density at the bond critical point) was 0.58. Aside from this weak bond and the strained nature of the S_3 ring, the *trans*-disulfoxide structure resembles very closely what one would expect from tetrahedral hybrids on the sulfur atoms, essentially as found in other sulfoxide species.[2] This would require, however, a strongly bent S1−S3 bond, which is not observed. Wong and Steudel have explained the weak bond in terms of the attractive $\pi^*-\pi^*$ interaction of the two low-lying SO moieties in HOMO orbitals. The associated six-electron, four-center MO and VB theories for this type of interaction are described in our ref 3 and in refs 6, 7, and 13 therein and is related to the wave functions for VB structures of the increased-valence type. Using increased-valence and Lewis-type valence VB structures, Harcourt[3] has studied these S_3O_2 species as well as N_2O_4 as O_2NNO_2, with a long, weak N−N bond.

In the present paper, we re-address the *trans*-disulfoxide structure from two other perspectives using the atoms-in-molecules (AIM)[4] and the electron localization function (ELF)[5−10] approaches. We also study the corresponding sulfone, O_2SSSO_2, which also has a fractional S1−S3 bond, (i.e., with a bond number or bond order which is less than unity; cf. ref 3) or “protocovalent”,[11] being very similar in nature to the weak N−N bond in O_2NNO_2. These results are in accord with what is obtained by inspection of the increased-valence VB structures.

Theoretical Basics

The two approaches used here to characterize the nature of bonding interactions are the delocalization index of Fradera, Austen, and Bader[12] based on the electron pair density in the atoms-in-molecules (AIM) approach[4] and electron localization function (ELF) isosurfaces and bond basin populations in the approach of Becke and Edgecombe[5] as extensively developed by Savin and Silvi and co-workers.[6,10] In this section, we outline the key ideas of these approaches.

Any scalar potential surface may be divided into disjoint regions (basins) based on the zero flux surfaces of its gradient field with the gradient paths ending at attractors within each subsystem. A readily envisioned example is the topology of a mountain range with its valleys defining the zero flux surfaces (lines) and the mountain peaks the attractors. In the AIM approach, atomic basins are derived from the scalar field of the electron density, $\rho(\vec{r})$, while ELF basins arise from a defined potential which is based on strong physical arguments regarding the Fermi hole[13,14] and the corresponding tendency of electron pairs to occupy different regions of space.

The Delocalization Index. Bader's approach[4] is based on the electron density, $\rho(\vec{r})$, a key observable in a molecule's description. The gradient field of the electron density is used to define atomic basins which can be integrated over to obtain AIM atomic basin electron populations. The delocalization index[12] is defined in terms of the electron pair density as it relates to the AIM atomic basins.

The electron pair density$P_2(\vec{r}_1,\vec{r}_2)$[13,14] is the diagonal part of the reduced second-order density matrix and may be integrated over two AIM basins, Ω_i and Ω_j, to obtain by definition the quantity N_{ij}, the interbasin pair number which can be written as

$$N_{ij} = N_iN_j - F_{ij} \qquad (1)$$

where N_i and N_j are the basin electron numbers, and this defines the quantity F_{ij}. It is the sum of the off-diagonal terms $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$ in the AIM approach that Fradera, Austen, and Bader[12] refer to as the delocalization index and use as a quantitative measure of the number of electron pairs shared between basins Ω_i and Ω_j; they also denote F_{ii} as the atomic localization index. The delocalization index represents the bond order only in that case where polarization effects are absent but is, nonetheless, a very useful indicator of electron pairs involved in the bond.

The nature of the delocalization index is more clearly seen when we express it for a closed-shell, single-determinant Hartree−Fock-

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10.1021/jp903098f CCC: \$40.75

like wave function, where it is given by integration of the exchange density over the two basins involved (cf. eq 2).

$$\delta_{ij} = 2F_{ij} = 4\sum_{\mu,\nu}^{\text{occ}} \langle\mu|\nu\rangle_i\langle\nu|\mu\rangle_j \qquad (2)$$

Here, standard bra-ket notation is employed, the subscripts i and j refer to basins Ω_i and Ω_j, and the Kohn−Sham orbitals from our calculations are employed. Since, strictly speaking, the electron pair density is not defined in density functional theory, our use of Kohn−Sham orbitals in eq 2 is an approximation.[15] Clearly, the delocalization index is nonzero only if (molecular) orbitals span (extend into) both basins i and j. It will tend to reflect more readily a "true" bond order when polarization effects are absent but will be more complicated when such effects are present. In the single-determinant approach, the delocalization index given in eq 2 is exactly the topological covalent bond order defined by Ángyán, Loos, and Mayer.[16] We think their term "covalent bond order" is quite appropriate.

The Electron Localization Function. ELF is a robust descriptor of chemical bonding based on the division of the electronic space into disjoint basins by a gradient field related to the Pauli exclusion principle. It can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle and allows one to define regions of space that are associated with different electron pairs in a molecule or solid. The position where ELF attains a maximum value (the attractor) can be used as an electron pair's signature.[17]

Using the vector field of the gradient of the electron localization function, the topology of the ELF function can be used to define basins within which one or more electron pairs are to be found.[18,19] ELF basins are labeled as either core or valence basins. Core basins contain a nucleus, while valence basins do not; hydrogen basins are taken as exceptions since, although they contain a proton, they represent a shared pair interaction. A valence basin is characterized by its number of connections to core basins, referred to as its synaptic order. Basins are connected if they are bounded by part of a common surface. A simple covalent bond basin would be connected to two core basins and would be of synaptic order two; a lone pair basin would be monosynaptic. More complex bonding basins can be polysynaptic. ELF is of special interest to chemists in that the resulting isosurfaces of ELF density tend to conform to the classical Lewis picture of bonding. Indeed, ELF has given quantitative credence to the valence shell electron pair repulsion (VSEPR) theory.[20,21] Note, too, that ELF surfaces are more complex than those of AIM, which yield only basins corresponding to "atoms".

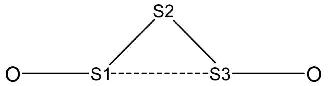
The population of a basin Ω_i, N_i, is given by integrating the total electron density, $\rho(\vec{r})$, over the basin volume (cf. eq 3).

$$N_i = \int_{\Omega_i} \rho(\vec{r})\mathrm{d}\vec{r} \qquad (3)$$

These populations are particularly important in that they tend to reflect delocalization effects and, in the case of bond basins in the absence of lone pairs, the bond order. Note that we use the same symbol, N_i, for both AIM and ELF basin populations, but the type of basin involved should be clear in context.

Details of the Calculations. General optimizations and minimum-confirming frequency calculations were carried out in the B3LYP/6-31+G(d),6d approach[22,23] with Gaussian 03.[24] The ELF analyses and AIM delocalization index calculations were performed employing the TopMod Package of Noury and co-workers,[25] also in the B3LYP/6-31+G(d),6d approach. Step sizes of 0.1 au and box sizes that extended 5.0 au from the outermost atomic coordinates in each direction were typically used.

TABLE 1: Structural Parameters for the S_3 Sulfoxide and Sulfone Species and Some Other Simple Representative Species in the B3LYP/6-31+G(d),6d Approach[a]



A. S_3 Sulfoxide and Sulfone Species

	trans-OS1S2S3O		$O_2S1S2S3O_2$
a. Geometrical Parameters[b]			
S1S2	2.156 Å	(2.136)	2.193 Å
S1S3	2.386	(2.354)	2.248
SO	1.488	(1.474)	1.462
angle S1S2S3	67.2°	(66.7°)	61.2°
dihedral OS1S2S3	108.2	(105.6)	107.6
b. ELF Basin Populations			
O lone pair	6.03		5.96
S1 lone pair	3.84		none
S2 lone pair	5.24		5.13
SO bond basin	1.21		1.49
S1S2 bond basin	3.84		1.68
S1S3 bond basin	(none)		3.04 (2)[c]
c. Bader Delocalization Indices			
SO	1.472		1.310
S1S2	1.078		0.868
S1S3	0.692		0.554

B. Geometries of Some Simple Representative R_2SO and R_2SO_2 Species

	H_2SO	H_2SO_2	C_2H_4SO	$C_2H_4SO_2$
SO	1.514 Å	1.464 Å	1.514 Å	1.474 Å
RS	1.390	1.373	1.864	1.771

[a] The S1−S3 weak bond is shown as a dashed line. [b] The best single configuration results (CCSD(T)/cc-pVTZ) of Wong and Steudel[1] are given in parentheses. [c] Total of two bond basins for the fractional or protocovalent bond.

Results and Discussion

Structural Data. Structural data for the trisulfide species and some other representative sulfoxides and sulfones are give in Table 1 and fit nicely into the general picture of these sulfur-containing compounds. As one adds additional oxygen atoms to the S1 and S3 atoms, the S−O bond lengths decrease as the bulky sulfur lone pairs are replaced by the more compact oxygen atoms, although this is not the decrease seen in the simpler species in part B of Table 1. The S1−S3 distance actually decreases in the sulfone as the S1−S2−S3 angle approaches 60°, although the Bader delocalization index decreases somewhat from 0.69 to 0.54.

ELF Basin Populations and the Weak S1−S3 Bond. The important focus here is on the nature of the weak S1−S3 bond in OSSSO and O_2SSSO_2. In both species, the bond length is considerably longer than what one might take for a conventional S−S single bond (Pauling covalent distance of about 2.08 Å). Indeed, the S1−S2 and S2−S3 bonds are also somewhat long due partly to the strain of the three-membered sulfur ring and also to the fractionality of these bonds (cf. Figures 2 and 3 of ref 3 for OSSSO).

The nature of the S1−S3 bond is best examined in terms of the associated ELF basin populations. These are illustrated nicely by the isosurfaces for the sulfoxide and sulfone shown in Figures 1 and 2. First, there is no S1−S3 bond basin as such in the

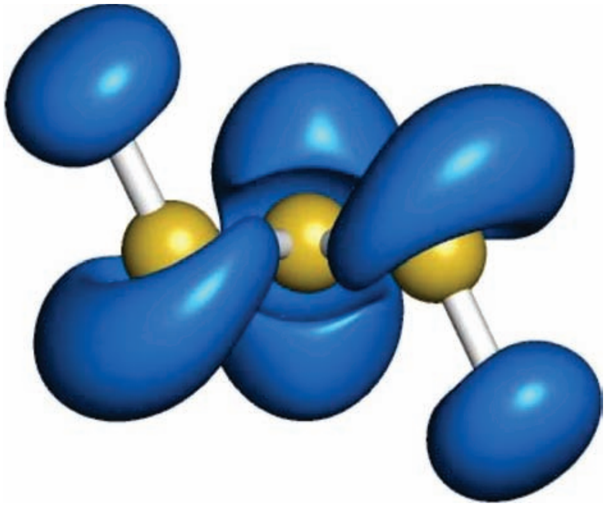


Figure 1. $\eta = 0.80$ ELF isosurface of OSSSO viewed perpendicular to the S1−S3 bond. Note the absence of any S1−S3 bond basin. The central S lone pairs are contained in the comma-shaped basin at the back, with the terminal S lone pair basins front left and right "below" the corresponding compact O lone pair basins.

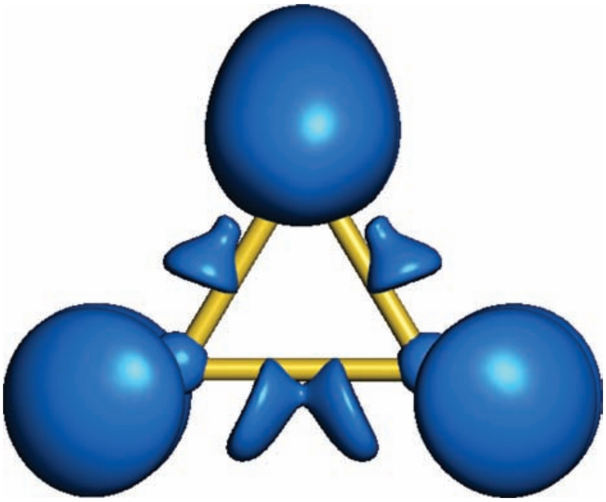


Figure 2. $\eta = 0.80$ ELF isosurface of O_2SSSO_2 viewed perpendicular to the SSS ring. Note the presence of two S1−S3 bond basins. The central S lone pair basin is viewed from the top at the top of the figure, along with two of the four O lone pair basins at the lower left and right.

sulfoxide (Figure 1), a clear indicator of the unusual and weak nature of this bond. In the sulfone (Figure 2), however, two bond basins are present near the midsection of the bond.

Figure 1 does indicate, however, that what are primarily the S1 and S3 lone pair basins do extend along the S1−S3 bond line. In saturated systems, ELF bond basins generally represent well the electron pair (or pairs, for multiple bonds) that characterize the method. It is remarkable the extent to which the ELF basin populations often agree with our notions of the number of electrons involved with bonding or in a lone pair. However, a flaw in the method is that ELF basin populations are not always straightforward due to delocalization/migration of the electrons among the various basins, especially when formally lone pair basins are nearby[6,11] and electron populations that might typically be of a bond nature are partially incorporated into the lone pair basins. We believe such is the case here for the S_3 sulfoxide.

While the S2 lone pair basin contains 5.24 electrons for two lone pairs, each of the S1 and S3 single lone pair basins in the sulfoxide has 3.84 electrons, an "excess" of about 1.22 electrons relative to the isolated sulfur lone pair basins. We believe this excess is associated with the S1−S3 bond and so argue by looking at the sulfone species.

There are, of course, no S1 nor S3 lone pairs in the sulfone, but Figure 2 clearly shows the presence of two bond basins along the S1−S3 bond line, each containing 1.52 electrons.

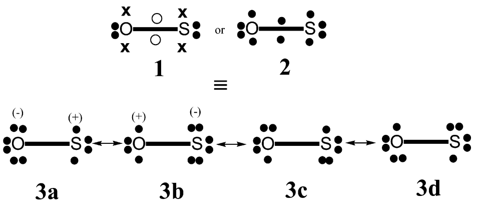
Fractional S−S Bonding. Although unusual, the presence of two "valence" basins along an internuclear axis has been seen before. In their study of elementary chemical processes by catastrophe theory, Krokidis, Noury, and Silvi[26] studied the C−C bond breaking in ethane. In its equilibrium configuration, there is, as expected, a single C−C bond basin. As that bond is stretched, the bond basin divides into two at an internuclear distance of 3.34 Å, a process that signals the breaking of the C−C bond leading to two methyl radicals. Llusar et al.,[11] in their topological analysis of electron-depleted homopolar chemical bonds, indicate that a similar result is found in N_2 upon dissociation and, more importantly, that such a dual bond basin character is present in F_2 at its equilibrium geometry. We have seen this, too, in the example of N_2O_4;[27] vide infra. F_2 has an anomalously small bond dissociation enthalpy compared to the higher-Z dihalides such as Cl_2, Br_2, and I_2.[28] Pertinent to the N_2O_4 case is the work of Fuster et al.[29] in their study of NO and its various neutral and charged dimers, where two N−N bond basins are present when the very weakly bound $(NO)_2$ dimer is formed. Llusar et al.[11] have referred to such bonds as "protocovalent".

For nearly 50 years, these types of bonds have also been recognized to be fractional. Their VB N−N bond numbers[30] or MO N−N bond orders (ref 17 of ref 3) are less than unity due to some delocalization of oxygen nonbonding electrons into singly occupied nitrogen AOs of the N−N bond (refs 4−13 and 17 of ref 3). In any case, for ONNO as O═N−N═O with C_{2v} symmetry, the origin of the long, weak N−N bond has been associated primarily[31] with the orientations of the nitrogen lone pair AOs and the associated strong nonbonded repulsions between the nitrogen atoms rather than to some delocalization (which does occur) of oxygen nonbonding electrons into the nitrogen N−N bonding AOs.

More recently,[27] it was observed that the bond basin populations for the N−N bond in N_2O_4 exhibit only modest changes as the NO_2 moieties are brought together to form the dimer molecule. Along the N−N bond line, there are two bond basins similar in appearance to the nitrogen valence basin in NO_2 and with populations only slightly reduced by about 0.4 electron (to 1.87) from the equivalent basins in each isolated NO_2 molecule (of 2.25). All of this is in accord with the calculated fractionality of the N−N bond of O_2NNO_2 (cf., for example, refs 4−17 of ref 3 and ref 31).

Valence Bond Structures for OSSSO and O_2SSSO_2. The above ELF and AIM treatments involve electron pair bonds (normal and fractional) and lone pairs of electrons. Many of the VB structures that are presented in this section also possess one-electron bonds. The atomic formal charges in the VB structures are assigned on the assumption that bonding electrons are shared equally by pairs of adjacent atoms. They are not the variationally best formal charges.

(a) SO and OSSSO. For the $^3\Sigma^-$ ground state of SO, the ($S = M_S = +1$ spin) VB structure is **1**[32] (cf. the Green−Linnett discussion for $^3\Sigma_g^-$ O_2)[33] in which the crosses and circles (× and ○) for the four $p_x(O)$, $p_x(S)$, $p_y(O)$, and $p_y(S)$ electrons and two $\pi_x(OS)$ and $\pi_y(OS)$ electrons represent electrons with m_s spin quantum numbers of +1/2 and −1/2, respectively.[32,33] When electron spins are not indicated, the resulting VB structure is **2**, which is equivalent to resonance between the Lewis structures **3a**−**3d**. This identity was used in ref 3 to deduce that the increased-valence structure **2** of Figure 2 of ref 3 and Figure 3 here is



equivalent to resonance between the 16 Lewis structures in Figure 3 of ref 3. Because of the absence of 1 or more S−S electron pair bonds in 15 of these Lewis structures, each of which is a singlet diradical (or long-bond) Lewis structure, the S−S bonds are fractional, that is, their bond numbers are less than unity.

In Figure 4, we show five types of VB structures for ═SO substituents. Types (a) and (b) are Lewis structures with electron pair bonds, without and with expansion of the sulfur valence shell (via the participation of a 3d AO as a hybridization function or valence AO). The type (c) structure is an increased-valence structure without sulfur 3d AO participation as a hybridization function. It is obtained (see, for example, refs 7, 8, 12, 14, and 16 of ref 3) either via type (a) → type (c) delocalizations of oxygen nonbonding electrons into O−S bonding MOs or by spin pairing the two odd (antibonding) electrons of $^3\Sigma^-$ SO with the two unpaired electrons of the ^3P ground state of a sulfur atom. These techniques were used to construct increased-valence structure **2** for OSSSO in Figure 2 of ref 3 and again in Figure 3 here. In these figures, VB structure **1** is the type (a) Lewis structure, and VB structure **3** represents the OS($^3\Sigma^-$) + S(^{3}P) + SO($^3\Sigma^-$) spin pairing process.

A type (d) Lewis VB structure is also displayed in Figure 4. It does not involve expansion of the sulfur valence shell and can be stabilized via a one-electron delocalization from the $X^{(-)}$ into an $X^{(-)}$−$S^{(+)}$ bonding MO to generate the type (e) increased-valence structure. Although this type of increased-valence structure contributes to the resonance schemes for OSSSO and O_2SSSO_2, it is not needed to provide the primary VB representations of the electronic structures of these molecules.

It should be noted that the type (a) → type (c) and type (d) → type (e) one-electron delocalizations of Figure 4, when determined variationally, are always stabilizing.

In ref 34, when discussing S−O double bonds for H_2SO_3 and H_2SO_4, consideration is not given to the possible use of SO VB structures of type (c) of Figure 4.

(b) O_2SSSO_2. For O_2SSSO_2, the standard Lewis structure of type (a) is **4** without expansion of the sulfur valence shell and approximately sp^3 hybridization for the S1 and S3 sulfur atoms. This VB structure involves (+2) formal charges on the S1 and S3 sulfur atoms. Four sets of type (a) → type (c) delocalizations generate increased-valence structure **5**, with zero formal charges on these atoms. This increased-valence structure involves two SO_2* excited states, each of which involves two five-electron, three-center bonding units (see the Appendix). The associated VB structure for SO_2* is **7**, which can be constructed from the ground-state VB structure **6** (with a nonpaired spatial orbital VB structure, $\dot{O}\cdot S\cdot \dot{O}$, for the distribution of the four π electrons) via the electron excitations shown in this structure.

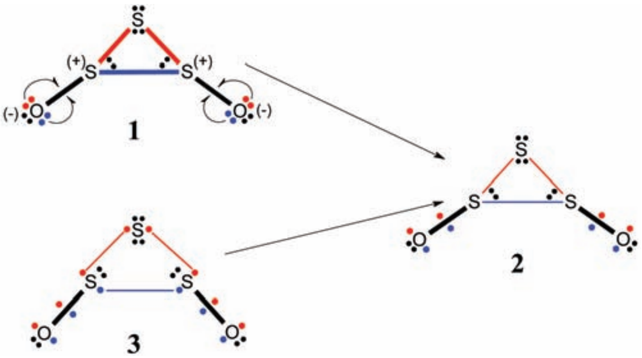


Figure 3. VB structures for OSSSO$^{(3)}$, with one 6-electron 4-center bonding unit (blue), and two 4-electron 3-center bonding units (red). **1** = standard Lewis. **2** = increased-valence. **3** = OS + S + SO.

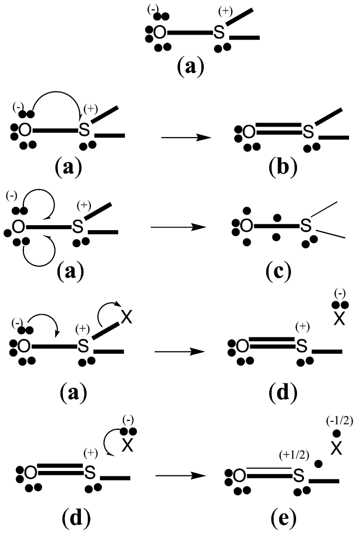
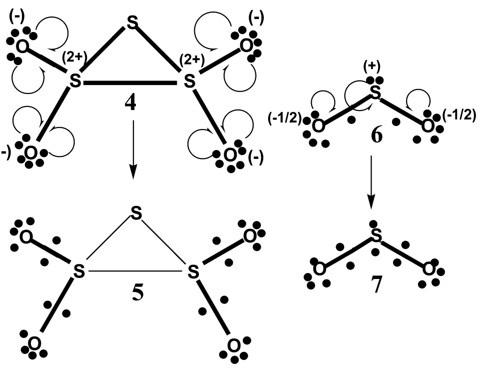


Figure 4. Types of VB structures for sulfoxide substituents. When the lone-pair on the sulfur atom of each sulfoxide VB structure is replaced by an electron-pair bond line, the sulfur atom of the resulting sulfone VB structure acquires an additional +ve formal charge, as occurs in Lewis structures **4** and **8** for O_2SSSO_2.



Other types of increased-valence structures, such as structure **9**, can be generated from the Lewis structure **8**, that is, from structure **4** above.

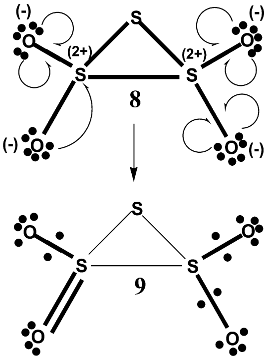


TABLE 2: B3LYP/6-31+G(d), 5d//B3LYP/6-31+G(d),6d d-Orbital Gross Orbital Populations

A. Trisulfur Compounds						
OSSSO	S1	0.224	S2	0.052	O	0.028
O_2SSSO_2	S1	0.491	S2	0.045	O	0.030
B. Some Representative Sulfoxides and Sulfones						
H_2SO	S	0.235	O	0.025		
H_2SO_2	S	0.540	O	0.029		
C_4H_2SO	S	0.237	O	0.025		
$C_4H_2SO_2$	S	0.540	O	0.029		

Four VB structures of type **9**, with expansion of the valence shell for one sulfur atom, are obtained from structure **8** via one type (a) → type (b) delocalization and three type (a) → type (c) delocalizations. These structures participate in resonance with structure **5** to imply that the S1 and S3 d-orbital populations are less than 0.5. (It has been known for some time[32] that the use of sulfur 3d AOs as hybridization functions in sulfur compounds is small.) Each of the five structures has fractional S−S bonds, which is in accord with the calculated lengths for O_2SSSO_2 being longer than single bonds.

In Table 2, we report gross orbital populations of sulfur d-orbitals for a number of sulfoxides and sulfones. The sulfone d-orbital populations are nearly twice what they are for the sulfoxides. Thus, the calculated S1 and S3 d-orbital populations are 0.491 for O_2SSSO_2 and 0.224 for OSSSO. (It is noted that the S2 d-orbital population is small for both species, 0.045 and 0.052, respectively.) These results, which are basis-set-dependent, suggest that the type (a) → type (b) delocalization is more relevant for O_2SSSO_2 than it is for OSSSO.

Summary

The weak S1−S3 bonds in the OSSSO *trans*-disulfoxide and the corresponding sulfone, O_2SSSO_2, have been re-addressed at the B3LYP/6-31+G(d) level using both the atoms-in-molecules (AIM) and the electron localization function (ELF) approaches. The S1−S3 bonds are clearly characterized as fractional (i.e., with a bond number or bond order which is less than unity) or protocovalent and are very similar in nature to the weak N−N bond in O_2NNO_2. The results are in accord with what is obtained by inspection of increased-valence VB structures.

Acknowledgment. D.B.C. is indebted to Duke University and the Center for Applied Computational Studies at East Carolina University for providing CPU time that allowed these calculations to be carried out and to Mr. W. Day and the Beratan research group for technical and computational assistance. R.D.H. thanks Dr. Stephen Best for modifying Figure 2 of ref 3 to obtain Figure 3.

Appendix

SO_2* VB structure 7. A simple way to demonstrate that the SO_2* VB structure **7** represents an excited state is initially to construct the MO configuration for 10 relevant electrons of the ground state. Six of these electrons are lone pair electrons that occupy three in-plane overlapping AOs, $a = n_O$, $b = n_S$, and $c = n_O$. There are four π electrons which occupy the AOs $d = \pi_O$, $e = \pi_S$, and $f = \pi_O$. The ground-state ($S = 0$ spin) MO configuration for these 10 electrons is given by eq A1

$$\Psi(SO_2) = (\psi_1)^2(\psi_2)^2(\psi_3)^2(\psi_4)^2(\psi_5)^2 \qquad (A1)$$

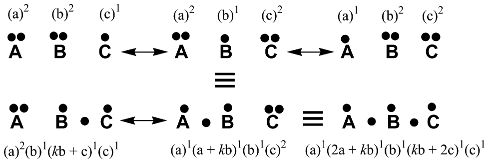


Figure 5. Types of VB structures for the 5-electron 3-center MO configuration $(\psi_1)^2(\psi_2)^2(\psi_3)^1$.

in which $\psi_1 = a + c + kb$, $\psi_2 = a - c$, $\psi_3 = k^*(a + c) - b$, $\psi_4 = d + f + Ke$, $\psi_5 = d - f$, and $\psi_6 = K^*(d + f) - e$ are orthogonal three-center MOs.

By exciting a ψ_3 electron into the vacant ψ_6 MO, we obtain the excited-state configuration given by eq A2

$$\Psi(SO_2^*) = (\psi_1)^2(\psi_2)^2(\psi_3)^1(\psi_4)^2(\psi_5)^2(\psi_6)^1 \qquad (A2)$$

which involves two five-electron, three-center bonding units, $(\psi_1)^2(\psi_2)^2(\psi_3)^1$ and $(\psi_4)^2(\psi_5)^2(\psi_6)^1$. (This type of configuration has been invoked in a discussion[35] of the bonding for an excited state of NO_2^- as a component of the Angeli's salt anion $N_2O_3^{2-}$.) On several occasions elsewhere,[36] it has been deduced that there are three equivalent VB representations for this type of bonding unit, namely, those of Figure 5 (for $(\psi_1)^2(\psi_2)^2(\psi_3)^1$).

In VB structure **7**, there are two $(a)^1(2a + kb)^1(b)^1(kb + 2c)^1(c)^1$ type VB representations. The a, b, and c electrons have parallel spins, which are opposed to those of the two electrons that occupy the nonorthogonal $2a + kb$ and $kb + 2c$ MOs.[36]

References and Notes

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JP903098F