Oxysulfur Compounds Derived from Dimethyl Disulfide: An ab Initio Study

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The optimized geometries of oxysulfur compounds derived from dimethyl disulfide were calculated at the MP2/6-31G* level, and the relative energies of isomers in the $CH_3S_2OCH_3$, $CH_3S_2O_2CH_3$, $CH_3S_2O_3CH_3$, and $CH_3S_2O_4CH_3$ series were compared. All these derivatives are characterized by long S−S bonds or long sulfenyl or sulfinyl S−O bonds for sulfur−oxygen-bridged isomers. According to the geometrical parameters calculated for *vic*-disulfoxide **4RR** in the $CH_3S_2O_2CH_3$ series, this compound is better described as two interacting sulfinyl radicals, and the obtained results substantiate the experimental scheme proposed by Clennan[28] for the intramolecular singlet oxygen addition on disulfides. The UV spectra of all these isomers were evaluated at a standard ab initio level: despite underestimated wavelengths, their evolution (wavelengths and molar extinction coefficients) is consistent with experiment and indicates a strong influence of the $\sigma_{S-S}, n_S \rightarrow \sigma^*_{S-S}$ transition for sulfur−sulfur-bridged isomers and of $n_S, n_O \rightarrow \sigma^*_{S-O}$ transitions for sulfur−oxygen-bridged isomers. As a result, these compounds will be cleaved photochemically by S−S or alternatively by sulfenyl or sulfinyl S−O bond cleavage, leading to oxysulfur radicals. The numerous experimental data on oxysulfur molecules and radicals are discussed in light of the predicted stability and photochemical reactivity of both classes of molecules. The validity of this standard method of evaluation of UV spectra was further assessed by a more accurate calculation on a known stable model compound, methyl methanethiosulfinate (**2**), by use of an extensive configuration interaction treatment (MRSDCI formalism).

Introduction

Athough investigated for a long time, oxidation reactions of thiols, disulfides, and sulfides with a variety of reagents[1−6] is still of current interest,[7] with a special consideration to photochemical oxidation.[8−14] One-electron oxidation of thiols RSH leads to disulfides RSSR **1a**, which may be further oxidized to higher oxidation products depending on the reaction conditions.[1] Sulfur−sulfur bond breaking leads through a one-electron process to sulfenic acids RSOH, whereas oxygen addition at sulfur may give rise to a variety of oxysulfur compounds. Among them, thiosulfinates[15] (sulfinothioic acid *S*-esters) RS(O)SR **2a**, thiosulfonates[16] (sulfonothioic acid *S*-esters) RS(O)$_2$SR **3a**, and *vic*-disulfones[17] RS(O)$_2$S(O)$_2$R **6a** may be considered as stable compounds, while sulfinyl sulfones RS(O)S(O)$_2$R **5a** readily undergo hydrolysis to sulfinic acids RSO$_2$H.[16] The ultimate oxidation products are the industrially important sulfonic acids RSO$_3$H.

A salient feature of the oxidation intermediates in the disulfide series is their easy interconversion through radicals formation as exemplified in the following experiments:

(a) Peroxy acid oxidation of disulfides and thiosulfinates:[18−25] unstable *vic*-disulfoxides RS(O)S(O)R **4a**, *OS*-

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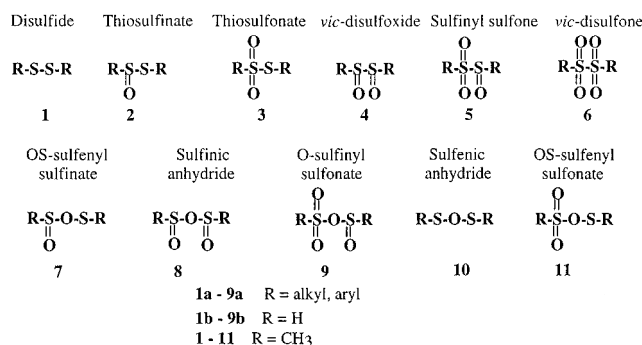(13) Banchereau, E.; Lacombe, S.; Ollivier, J. *Tetrahedron* **1997**, *53*, 2087−2102.

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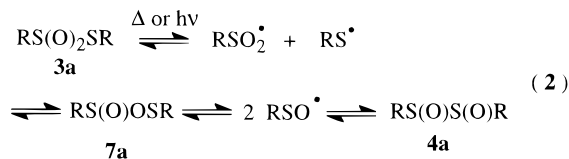
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Disulfide	Thiosulfinate	Thiosulfonate	*vic*-disulfoxide	Sulfinyl sulfone	*vic*-disulfone
R-S-S-R	R-S-S-R	R-S-S-R	R-S-S-R	R-S-S-R	R-S-S-R
1	**2**	**3**	**4**	**5**	**6**

OS-sulfenyl sulfinate	Sulfinic anhydride	O-sulfinyl sulfonate	Sulfenic anhydride	OS-sulfenyl sulfonate
R-S-O-S-R	R-S-O-S-R	R-S-O-S-R	R-S-O-S-R	R-S-O-S-R
7	**8**	**9**	**10**	**11**

1a - 9a R = alkyl, aryl
1b - 9b R = H
1 - 11 R = CH$_3$

sulfenyl sulfinates RS(O)OSR **7a**, and sulfinic anhydrides RS(O)OS(O)R **8a** have been characterized.

$$RSSR' \xrightarrow{[O]} RS(O)SR'$$
$$\textbf{1a} \qquad \textbf{2a}$$

$$(1)$$
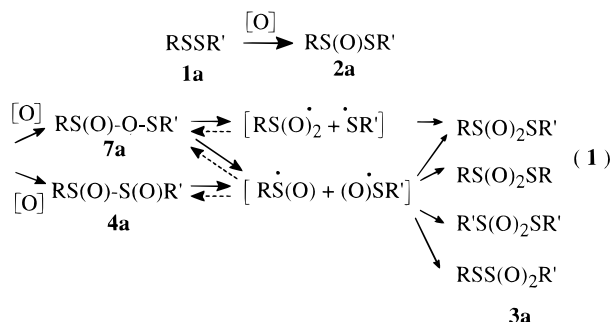
Other thermally or photochemically induced interconversion between molecular compounds 4a, 7a, and 3a through formation–recombination of sulfinyl RSO•, sulfonyl RSO₂•, and thiyl RS• radicals are well-known.[16,22–24,26,27]

$$RS(O)_2SR \underset{}{\overset{\Delta \text{ or } h\nu}{\rightleftharpoons}} RSO_2^{\bullet} + RS^{\bullet}$$
$$\textbf{3a}$$
$$\rightleftharpoons RS(O)OSR \rightleftharpoons 2\ RSO^{\bullet} \rightleftharpoons RS(O)S(O)R \qquad (2)$$
$$\textbf{7a} \qquad\qquad\qquad\qquad \textbf{4a}$$

(b) Photooxidation of disulfides with singlet oxygen for which a unimolecular process was demonstrated:[28,29] *vic*-disulfoxides **4a** and related isomers **12a** and **13a**, as well as sulfinyl radicals CH$_3$SO•, have recently been proposed as possible intermediates (eq 3).

(c) Reaction of sulfinyl with sulfonyl radicals (eq 4) and disproportionation of sulfonyl radicals (eq 5), which are put forward to account for the obtained sulfonyl derivatives or for the observation of sulfinyl radicals[22,30–34] (eq 5). It should be borne in mind that in the RS$_2$O$_3$R series,

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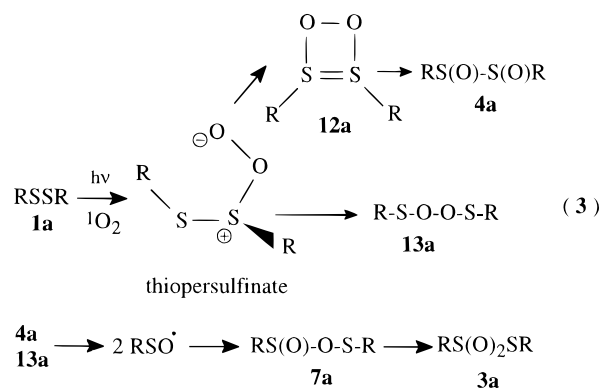
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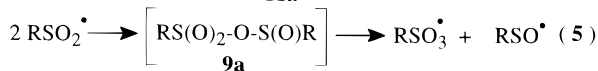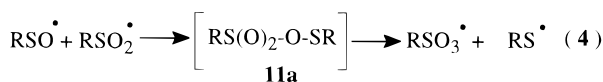
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$$RSSR \xrightarrow[^1O_2]{h\nu} \cdots \rightarrow RS(O)\text{-}S(O)R \qquad \textbf{4a}$$
$$\textbf{1a}$$
$$\rightarrow R\text{-}S\text{-}O\text{-}O\text{-}S\text{-}R \qquad (3)$$
$$\textbf{13a}$$

thiopersulfinate

$$\begin{matrix}\textbf{4a}\\\textbf{13a}\end{matrix} \longrightarrow 2\ RSO^{\bullet} \longrightarrow RS(O)\text{-}O\text{-}S\text{-}R \longrightarrow RS(O)_2SR$$
$$\textbf{7a} \qquad\qquad \textbf{3a}$$

only sulfinyl sulfone **5a** and sulfinic anhydride **8a** have been identified[35,36] and not *OS*-sulfenyl sulfonate **11a**, while in the RS$_2$O$_4$R series *vic*-disulfone **6a** is claimed to be favored over its unknown isomer *O*-sulfinyl sulfonate **9a**.[16]

$$RSO^{\bullet} + RSO_2^{\bullet} \longrightarrow \left[RS(O)_2\text{-}O\text{-}SR \right] \longrightarrow RSO_3^{\bullet} + RS^{\bullet} \quad (4)$$
$$\textbf{11a}$$

$$2\ RSO_2^{\bullet} \longrightarrow \left[RS(O)_2\text{-}O\text{-}S(O)R \right] \longrightarrow RSO_3^{\bullet} + RSO^{\bullet} \quad (5)$$
$$\textbf{9a}$$

(d) The solution photooxidation of dimethyl disulfide with molecular ground-state oxygen, which leads to methanesulfonic acid, along with sulfuric acid:[12–14] The proposed mechanism[37] postulates the formation of the photochemically reactive methyl methanethiosulfinate (**2**), *OS*-sulfenyl sulfinate **7**, dimethyl sulfinyl sulfone **5** (or alternatively sulfinic anhydride **8**), and *O*-sulfinyl sulfonate **9**, besides the detected intermediates methanesulfinic acid CH$_3$SO$_2$H and methyl methanethiosulfonate **3**.

(e) In the atmospheric photooxidation of methyl sulfide and dimethyl disulfide, which are anthropogenic pollutants and atmospheric constituents of biogenic origin:[38] Methanesulfonic acid RSO$_3$H and inorganic sulfates are also always produced.[39] Radical species such as meth-

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anethiyl $CH_3S^•$, methanethiylperoxyl $CH_3SOO^•$, methanesulfinyl $CH_3SO^•$, and methanesulfonyl $CH_3SO_2^•$ radicals appear to be involved in these oxidation processes. Chatgilialoglu proposed a tentative mechanism where the formation of a weak adduct between a thiyl and a peroxythiyl radicals should lead to two sulfinyl radicals:[40]

$$CH_3SOO^• + CH_3S^• \longrightarrow [CH_3SOOSCH_3] \longrightarrow 2\ CH_3SO^•\ (\mathbf{6})$$
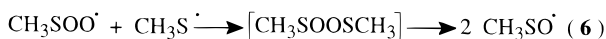
From this whole set of data, it appears that various oxysulfur molecules, and not only the experimentally characterized ones, have to be put forward to explain the observed reactivity. Accordingly, the following questions remain to be addressed: What are the relative energies of isomers in a series, namely $CH_3S_2OCH_3$, $CH_3S_2O_2CH_3$, $CH_3S_2O_3CH_3$, $CH_3S_2O_4CH_3$? What are the main geometrical features of these molecules? How can calculated UV spectra account for the photochemical reactivity of this class of compounds and allow a better understanding of the experimental mechanistic schemes previously described?

We thus analyzed, for all the possible oxysulfur isomers in each series, within the same ab initio calculation level (MP2/6-31G*), their electronic structure related to their optimized geometrical parameters. For the sake of completeness, we involved in this study three unknown compounds: *OS*-methyl thioperoxymethanesulfenate (dimethylsulfenic anhydride) **10** as a possible isomer of thiosulfinate **2** in the $CH_3S_2OCH_3$ series, *OS*-methyl thioperoxymethanesulfenate (*OS*-sulfenyl sulfonate) **11** in the $CH_3S_2O_3CH_3$ series, and *O*-methylsulfinyl methanesulfonate (sulfinyl sulfonate) **9** in the $CH_3S_2O_4CH_3$ series. This analysis allows the comparison of the energies of all the possible isomers in a series. Except for disulfoxide **4**, only the most stable conformations are described for each isomer (a full conformational analysis is out of the scope of this study). From these data, a comparative evaluation of the UV spectra of these molecules was carried out at a standard calculation level (CIS/6-31G*). This simple approach allows a better understanding of the photochemical reactivity of both known stable molecules (**1**–**3** and **6**) and of assumed oxidation intermediates (**4**, **5**, **7**–**9** and **11**). However, to assess the calculation method, we performed a more elaborate calculation on a model stable molecule, namely *S*-methyl methanesulfinothioic acid (**2**) (methyl methanethiosulfinate), the UV[13,41–42] and photoelectron[43] spectra of which are known. From this high-level calculation, we could appreciate first the accuracy of this second methodology to calculate the UV and photoelectron spectra of stable compounds and second the validity of the qualitative evaluation of the UV spectra of the whole set of molecules within the standard method (CIS/6-31G*).

Computational Methods

Geometry optimization (MP2/6-31G* level) and first UV spectra evaluation on these optimized geometries, taking into account in the configuration interaction scheme only single

excited states (CIS/ 6-31G*), were performed with the Gaussian92 quantum mechanical package developed by Pople and co-workers.[44]

More elaborate calculations with extensive configuration interaction were carried out with the CIPSI algorithm developed by Malrieu and co-workers[45,46] on a model stable molecule, methyl methanethiosulfinate (**2**) in its MP2/6-31G*-optimized geometry. The 6-31G* basis set was still used. A multideterminantal zero-order wave function was built from an iterative selection of the most important determinants, derived from the complete set of canonicals orbitals. This S_0-subspace includes about 400 determinants and was submitted to a second-order perturbational treatment. Then, on the M-subspace including S_0 plus the single and double excitations of S_0 that had the highest second-order perturbational contributions (this M-subspace is about 50 000 determinants), a variational procedure was performed. Ultimately, the MP2 energetic part of the latest generated configurations that was not included in the M-subspace was added to the corresponding variational energy: the obtained results refer to the MRSDCI label.

Different calculations were carried out first on the ground state and then on the five first monoexcited singlet states and three first ionic states within the same ground-state optimized geometry (vertical transitions). From the energetic differences with the ground state, the first transitions of the UV spectrum[13] and the first three bands of the photoelectron[43] spectrum may be reached.

Results

I. Geometrical and Energy Data. The optimized MP2/6-31G* geometric parameters of the studied compounds are presented in Table 1 for S−S-bridged compounds and in Table 2 for their S−O−S-bridged isomers. (Only relevant data are given here; the complete geometric values are available in the Supporting Information.) For the whole set of studied compounds the important geometrical parameters are the S−S, or alternatively the single O−S, bond lengths. The dihedral angle around sulfur is of particular significance for unoxidized species such as disulfide **1**, as it is related to the electronic repulsion between sulfur lone pairs. This repulsion is less important for compounds bearing a sulfinyl moiety and totally disappears for sulfonyl derivatives as sulfur is fully oxidized.

The energetic difference with the most stable isomer in each series is reported in Table 3. In the following, we shall discuss first the geometries of compounds with a S−S bond (**1**–**6**) and second the geometries of sulfur−oxygen−sulfur-linked compounds (**7**–**11**).

Our results can be compared with experimental geometries of related compounds only for dimethyl disulfide (**1**), thiosulfinate **2**, and *S*-methyl methanesulfonothioate (methyl methanethiosulfonate) (**3**) (Table 1). For disulfide **1** our calculated S−S bond length (2.055 Å) and CSSC dihedral angle (85.06°) are in good agreement with the experimental values (2.022 Å and 83.9° [47] or 2.04 Å

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Table 1. Geometrical Parameters of S−S Bridged Isomers. Numbering of Atoms: $H^3C_7S_1(O)_3(O)_4S_2(O)_6(O)_5C_8H^3$

	1 (exp)	**2** (exp)[a]	**3** (exp)[b]	**4RR** form 1[c]	**4RR** form 2	**4RS** meso	**5**	**6**[d] (exp)[e]
S_1-S_2	2.055 (2.022[47]) (2.04[48])	2.161 (2.108)	2.101 (2.091)	2.690	2.744	2.303	2.262	2.210 (2.193)
S_1-O_3		1.506 (1.457)	1.463 (1.448)	1.526	1.554	1.510	1.473	1.469 (1.428)
S_1-O_4			1.468 (1.443)				1.472	1.469 (1.428)
S_2-O_5				1.526	1.554	1.510	1.509	1.469 (1.428)
$C_7S_1S_2C_8$	85.06 (83.9)[47] (84.7)[48]	77.35	83.52	243.33	160.95	179.96	154.47	180

[a] R = pCH$_3$C$_6$H$_4$.[51] [b] R = pBrC$_6$H$_4$.[53] [c] C_2 symmetry. [d] C_{2h} symmetry. [e] R = C$_6$H$_5$.[55]

Table 2. Geometrical Parameters of Sulfur−Oxygen−Sulfur-bridged Isomers. Numbering of Atoms: $H^3C_7S_1(O)_4(O)_6O_3S_2(O)_5C_8H^3$

	10[a]	**7**	**8**[b]	**11**	**9**
S_1-O_3	1.712	1.739	1.726	1.674	1.664
S_2-O_3	1.712	1.708	1.747	1.722	1.772
S_1-O_4		1.486	1.491	1.457	1.453
S_1-O_6				1.460	1.460
S_2-O_5			1.490		1.487
$S_1O_3S_2$	115.25	112.20	114.64	111.93	115.23
$C_8S_2O_3S_1$	80.42	93.54	−174.12	92.93	176.73

[a] C_2 symmetry. [b] RS isomer (no symmetry) as the RR isomer is calculated to be 2.3 kJ·mol^{-1} less stable.

Table 3. MP2/6-31G* Energetic Differences between Isomeric Compounds

series	isomer	ΔE (kJ·mol^{-1})
H$_3$CS$_2$OCH$_3$	H$_3$CS(O)SCH$_3$ (**2**)	0
	H$_3$CSOSCH$_3$ (**10**)	18.37
H$_3$CS$_2$O$_2$CH$_3$	H$_3$CS(O)$_2$SCH$_3$ (**3**)	0
	H$_3$CS(O)OSCH$_3$ (**7**)	47.70
	H$_3$CS(O)S(O)CH$_3$	
	4RR form 1	89.74
	4RR form 2	91.11
	4RS meso	111.81
H$_3$CS$_2$O$_3$CH$_3$	H$_3$CS(O)$_2$OSCH$_3$ (**11**)	0
	H$_3$CS(O)OS(O)CH$_3$ (**8**)	49.73
	H$_3$CS(O)$_2$S(O)CH$_3$ (**5**)	90.41
H$_3$CS$_2$O$_4$CH$_3$	H$_3$CS(O)$_2$OS(O)CH$_3$ (**9**)	0
	H$_3$CS(O)$_2$S(O)$_2$CH$_3$ (**6**)	70.28

and 84.7° [48]) and with the previous theoretical result of Benassi[49] (2.053 Å and 86.99°). For thiosulfinate **2**, we obtain, as Benassi and al. within the same method,[50] a rather long S−S bond length (2.161 Å) compared to the experimental value on an aromatic derivative (2.108 Å[51]) and to previous different evaluations (2.094 Å, SCF/6-31G* calculation,[49] or 2.097 Å, MCSCF/3-21G* calculation[52]). For thiosulfonate **3**, our calculated geometry is similar to the experimental one of an aromatic derivative: 2.101 for 2.091 Å[53] for the S−S bond length. On the whole, for these three compounds, S−S, S−O, and C−S bond lengths are sligthly overestimated by the MP2/6-31G* calculation.

An interesting feature concerns dimethyl *vic*-disulfoxide **4**, for which two diastereoisomers were studied, the

RR and the *RS* ones (Figure 1). For the least stable RS diastereoisomer, the meso form was found to be the most favored conformer as already mentioned.[49,52] However, our MP2/6-31G* S−S (2.303 Å) and S−O (1.510 Å) bond lengths are much longer than the SCF/6-31G* ones (2.147 and 1.480 Å)[49,52] and the HF/3-21G* ones for the parent compound **4a** (2.144 and 1.484 Å for both *RR* and *RS* diastereoisomers).[54] For the RR diastereoisomer, two strikingly different conformers were obtained with very long S−S bond lengths: 2.690 Å (form 1) and 2.744 Å (form 2). Previous calculations at the SCF/6-31G* level gave a bond length between 2.156 and 2.164 Å for this *RR* isomer.[49] For form 1, the S−O bond lengthens to 1.526 Å together with one of the C−H bonds (1.109 Å to 1.092 Å usually). A short H$_9$−O$_3$ and H$_{10}$−O$_5$ distance is thus calculated (1.948 Å) associated with small OSS (101.65°) and dihedral CSSO (10.30°) angles, evidencing significant hydrogen bonding. This conformer 1 may thus be described as a complex between two close sulfinyl radicals held by sulfur−sulfur interaction and hydrogen bonding with oxygen.

The geometry of form 2 is different as both S−O (2.744 Å) and S−O (1.554 Å) bond lengths are longer, whereas an interaction between the two oxygen is pointed out by a short O−O distance (2.134 Å) and reduced OSS (78.46°), OOS (101.06°), and dihedral OSSO angles (8.30°). It is interesting to note that exactly the same geometry was optimized starting from a disulfenic peroxide H$_3$CS−O−O−SCH$_3$ **13a**. This conformer **2** may thus be described as a complex between two sulfinyl radicals where both sulfur−sulfur and oxygen−oxygen interactions occur, i.e., similar to the cyclic intermediate **12a** proposed by Clennan for the singlet oxygen addition on disulfides[28] (eq 3). In other words, in this equation, **RR4a**, **12a**, and **13a** are found to have the same optimized geometry and should lead very easily, owing to the length of the S−S bond, to sulfinyl radicals as suggested by Clennan and al. The formation of such a complex is also in agreement with the proposal of Chatgilialoglu[40] for the gas-phase oxidation of thiyl radicals (eq 6).

In the CH$_3$S$_2$O$_3$CH$_3$ series, methylsulfinyl methyl sulfone (sulfinyl sulfone) (**5**) is also calculated with a long S−S bond (2.262 Å) while the other C−S and S−O bond lengths are consistent with the previous results on **2** or **3**. To our knowledge, no experimental data are available for sulfinyl sulfones.

(48) Sutter, D.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsch., Teil A* **1976**, *20*, 1676−1681.

(49) Benassi, R.; Fiandri, G. L.; Taddei, F. *THEOCHEM* **1993**, *279*, 239−252.

(50) Benassi, R.; Fiandri, G. L.; Taddei, F. *J. Org. Chem.* **1995**, *60*, 5855−5860.

(51) Kiers, C. Th.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 166−170.

(52) Benassi, R.; Fiandri, G. L.; Taddei, F. *Tetrahedron* **1994**, *50*, 12469−12476.

(53) Noordik, J. H.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 156−160.

(54) Freeman, F.; Angeletakis, C.; Pietro, W.; Hehre, W. *J. Am. Chem. Soc.* **1982**, *104*, 1161−1165.
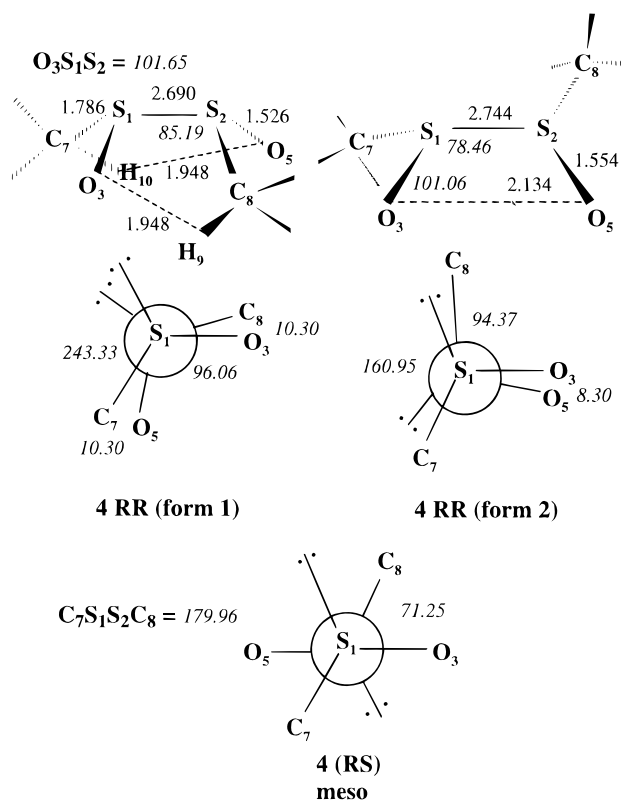
Figure 1. MP2/6-31G* optimized geometrical parameters of disulfoxide **4** (distances in Å, angles in deg in italicized characters).

The S−S bond length of dimethyl *vic*-disulfone **6** is only slightly smaller: 2.21 Å. This value appears in good agreement with the experimental one on an aromatic derivative: 2.19 Å.[55]

For these compounds bearing a S−S bond, a parallel between calculated S−S bond lengths and experimental bond dissociation energies may be drawn, further confirming the consistency of the calculated bond lengths (Table 4, Figure 2). In this figure, data on aromatic derivatives have been included. As the bond dissociation energies in this series are always weaker than in the aliphatic series,[15] they cannot be directly compared. However a common trend is observed: the shorter the S−S bond length, the higher the dissociation energy, with different correlation slopes between the aliphatic and aromatic compounds. Moreover, the ease of dissociation follows Kice's ordering[16] and weak S−S bonds are related to the presence of a sulfinyl group.[26] This result has been accounted for by Kice by the enhanced stability of sulfinyl radicals. A discrepancy for thiosulfinate **2a** is to be noticed: its weak bond dissociation energy (142 kJ·mol⁻¹) appears to be rather low. At last, if the calculated bond lengths for disulfoxide **4** (2.303 to 2.744 Å) are correct, it may be predicted to have a very weak bond dissociation energy, accounting for its difficult experimental characterization.

The geometrical parameters obtained for sulfur−oxygen−sulfur-linked molecules are summarized in Table 2. For comparison, the calculated bond lengths of alkyl derivatives of sulfur oxyacids in different formalisms are given in Table 5.

(55) Kiers, C. Th.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 126−132.

Table 4. Comparison between Experimental and Calculated Bond Lengths and Correlation with Experimental Bond Dissociation Energy

| compd | S−S bond length (Å) | | bond dissociation energy (kJ·mol⁻¹) |
	exptl	calcd[a]	
RSSR			
1, R = CH₃	2.04[48]	2.055	313[64]
1a, R = C₆H₅	2.03[66]		230[15]
RS(O)SR			
2, R = CH₃		2.161	192[64]
2a, R = *p*-CH₃C₆H₄	2.108[51]		142[15,65]
RS(O)₂SR			
3, R = CH₃		2.101	284[15,65]
3a, R = *p*-BrC₆H₄	2.091[53]		
RS(O)S(O)R			
4, R = CH₃		*RS* 2.147[49]	*b*
		RS 4.313[52]	
		RS 2.303	
		RR 2.156−2.164[49]	
		RR 2.690 (form 1)	
		RR 2.744 (form 2)	
RS(O)₂S(O)R			
5, R = CH₃		2.262	
5a, R = C₆H₅			117[65]
RS(O)₂S(O)₂R			
6, R = CH₃		2.210	
6a, R = C₆H₅	2.19[55]		171.4[65]

[a] This work unless otherwise stated. [b] 4.2 kJ·mol⁻¹ calculated from ref 52 for a 4.313 Å S−S bond length.
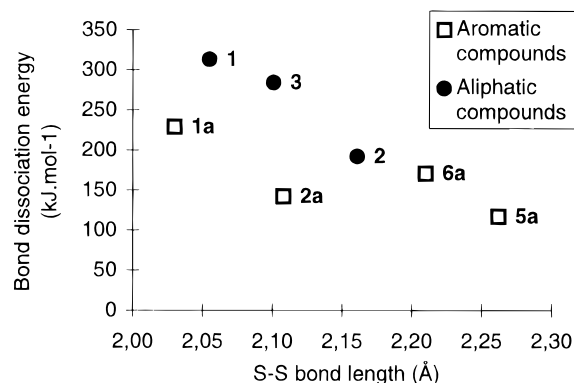

Figure 2. Correlation between calculated bond lengths (this work) and experimental bond dissociation energies (values in Table 4).

Table 5. Calculated S−O Bond Lengths of Alkyl Derivatives of Sulfur Oxyacids

compd	CH₃SOCH₃	CH₃S(O)OCH₃	CH₃S(O)₂OCH₃
MP2/6-31G* S−O bond length	1.690	1.684	1.636
RHF/6-31G* S−O bond length[56]	1.651	1.629	1.579

(a) For the five molecules **7**−**11** the angle at the central oxygen varies between 111 and 115°. The CSOS dihedral angle of sulfenates **10**, **7**, and **11** is always found around 90° like the CSSC dihedral angle of disulfide, indicating a gauche conformation in order to minimize the repulsion between lone pairs of sulfur and oxygen.

(b) The sulfenyl S−O bond length varies between 1.708 Å (**7**), 1.712 Å (**10**), and 1.722 Å (**11**), while it is 1.690 Å for methyl methanesulfenate H₃C−S−O−CH₃ (Table 5).

(c) The length of a single S(O)−O bond of sulfinyl compounds is longer: 1.739 Å for **7**, 1.726−1.747 Å for sulfinic anhydride **8**, and 1.772 Å for **9**. This bond length was estimated to 1.684 Å for methyl methanesulfinate H₃CS(O)OCH₃ (Table 5).

(d) The length of a single $S(O)_2-O$ bond of sulfonate is the shortest: 1.674 Å for **11**, 1.664 Å for **9**. This bond length was estimated to 1.636 Å for methyl methanesulfonate $H_3CS(O)_2OCH_3$ (Table 5).

From Table 5, it may be concluded that MP2/6-31G* bond lengths are slightly higher than in the RHF/6-31G* formalism, as already observed. However, it appears that the MP2/6-31G* calculated S–O bond lengths of the sulfenyl or sulfinyl derivatives of sulfur oxyacids are longer than that of their alkyl counterparts. Moreover, as for S–S bridged compounds, the presence of a sulfinyl group lengthens the corresponding $S(O)-O$ bond as compared to that of sulfenates, while the presence of a sulfonyl group shortens the $S(O)_2-O$ bond. The former effect no longer holds true for the alkyl esters as the sulfinate bond length is slightly smaller than the sulfenate bond length, the sulfonate bond length remaining the shortest.

From the energetic point of view (Table 3), in the $CH_3S_2OCH_3$ series, thiosulfinate **2** is, as expected, found to be more stable than sulfenic anhydride **10** but, surprisingly, by only a very small amount (18.37 kJ·mol^{-1}), close to the energetic difference recently obtained between **2** and **10** (27.5 kJ·mol^{-1}) on the same MP2(full)/6-31G*-optimized geometries.[57]

As already reported by Freeman[54] on the parent compound **3b** and assumed from its great experimental stability, thiosulfonate **3** is the most stable of the $CH_3S_2O_2CH_3$ isomers. However, the reduced energetic difference (47.7 kJ·mol^{-1}) with *OS*-methyl thioperoxymethanesulfinate (*OS*-sulfenyl sulfinate) (**7**) is in agreement with the experimentally observed easy interconversion **3a** ⇌ **7a** and with the statement that *OS*-sulfenyl sulfinates are probable coupling products between either two sulfinyl (RSO•) or one thiyl (RS•) and one sulfonyl (RSO₂•) radicals (vide supra, eq 2).[26] Moreover, the experimental reactivity is indicative of two possible S–O bond cleavages for *OS*-sulfenyl sulfinate **7**, either leading to two sulfinyl radicals or to one thiyl and one sulfonyl radical. This behavior may be accounted for by the two long S–O bond lengths calculated for **7**, resulting in rather weak S–O bonds.

In this family, disulfoxide **4** is less stable, by at least 89.74 kJ·mol^{-1}, but this energetic difference is much smaller than the one calculated by Freeman between parent **3b** and **4b** (221 kJ·mol^{-1}).[54] It is, however, interesting to note that both conformers (forms 1 and 2) of the *RR* diastereoisomer are markedly more stable than the meso *RS* diastereoisomer, by 22.07 and 20.07 kJ·mol^{-1}, respectively, despite their long S–S bond length (the longest of the whole set of studied molecules, Table 1). This probably reflects the stabilization arising from the formation of a complex between two sulfinyl radicals either through sulfur–sulfur interaction and hydrogen bonding (form 1) or from sulfur–sulfur and oxygen–oxygen interactions (form 2).

It should be recalled at this point that very different results were obtained by Benassi and al. for disulfoxide **4** depending on the calculation method. The energetic difference between the *RS* and the *RR* isomers at the SCF/6-31G* level[49] amounted only to 2 kJ·mol^{-1} in favor

(56) Hoz, T.; Basch, H. In *The Chemistry of Sulphur Containing Functional Groups, Suplement S*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: Chichester, 1993; pp 2–100.

(57) Hung, W. C.; Shen, M.; Lee, Y. P.; Wang, N. S.; Cheng, B. M. *J. Chem. Phys.* **1996**, *105*, 7402–7411.

of the *RS* diastereoisomer, and both diastereoisomers had similar, noticeably shorter S–S bond lengths (2.147 Å for **4RS** and 2.156–2.164 Å for **4RR**). With a multiconfigurational treatment (MCSCF/3-21G*) including the σ^*_{S-S} orbital in the valence active space, these authors obtained for **4RS** a strongly lengthened S–S bond (4.313 Å).[52] According to them, this implies that **4RS** is better described as two isolated fragments and that these two fragments are more stable than the disulfoxide molecule. The MP2/6-31G* S–S bond lengths, obtained through a pertubational treatment, are intermediate between the SCF/6-31G* and the MCSCF/3-21G* ones. This whole set of results is indicative of the influence of the σ^*_{S-S} orbital on the calculated geometrical parameters.

For $CH_3S_2O_3CH_3$ compounds, the obtained stability order is surprising. Indeed, the unknown molecule *OS*-sulfenyl sulfonate **11** is found to be the most stable, followed by *O*-methylsulfinyl methanesulfinate (sulfinic anhydride) (**8**) (ΔE = 49.73 kJ·mol^{-1}), the least stable by 90.41 kJ·mol^{-1} being sulfinyl sulfone **5**. Although sulfinyl sulfone **5** has been claimed to be thermodynamically favored over sulfinic anhydride, there are several cases where the sulfinic anhydride structure is preferred.[36] It is worth noting that in the low-temperature experiments carried out by Freeman and Angeletakis[18,21] alkyl sulfinic anhydrides **8a**, probably arising from the oxidation of sulfenyl sulfonate **7a**, were detected between −40 and −20 °C, but not sulfinyl sulfones **5a**. Sulfinic anhydrides **8a** can be stable up to 0 °C, depending on the alkyl rest, indicating some stability of these isomers. According to Kice,[16] "the actual difference in free energy between the two isomers (sulfinic anhydrides and sulfinyl sulfones) is not likely to be large". From our results, an energetic difference amounting to 40.68 kJ·mol^{-1} is obtained between the two isomers, but in favor of sulfinic anhydride **8**.

As in the $CH_3S_2O_3CH_3$ series, among the two $CH_3S_2O_4CH_3$ molecules the one with a sulfonate functional group, namely *O*-sulfinyl sulfonate **9**, is found to be substantially more stable than its disulfone isomer **6** (by 70.28 kJ·mol^{-1}). This result is in disagreement with Kice's statement:[16] for *vic*-disulfones, "as with the other anhydrides of sulfur oxyacids, the isomer with the sulfur–sulfur bond is thermodynamically more stable than the one with the oxygen bridge between the two sulfur atoms".

On the whole, within the MP2/6-31G* method, energetic differences between isomers appear reduced relative to HF/6-31G* estimation.[54] Our stability order is consistent with experiment for $CH_3S_2O_2CH_3$ isomers. For $CH_3S_2O_3CH_3$ and $CH_3S_2O_4CH_3$ compounds, our calculated results disagree with experimentally deduced thermodynamical data, although rather small energetic differences are calculated. This point will be further addressed in the following discussion.

II. Electronic Structures. The molecular orbital description is of particular significance to understand the origins of the UV transitions. The following symbols have been used: σ_{S-S} and σ^*_{S-S} stand for bonding and antibonding σ-type orbitals between sulfurs and n_S and n_O for lone pairs on sulfur and oxygen, respectively. For sulfur–sulfur-bridged compounds (Figure 3), the important observations are as follows:

(a) For all the molecules (**1**–**6**), the LUMO is an antibonding σ^*_{S-S} orbital. Its energy is particularly low when a sulfinyl group is present: 2.72 eV for thiosulfinate **2**, 1.80 eV for sulfinyl sulfone **5**, and especially 0.097 eV

	1	2	3	4 (RR)	5	6
S-S	CH_3SSCH_3	$CH_3S(O)SCH_3$	$CH_3S(O)_2SCH_3$	$CH_3S(O)S(O)CH_3$	$CH_3S(O)S(O)_2CH_3$	$CH_3S(O)_2S(O)_2CH_3$
bond length (Å)	2.055	2.161	2.101	2.690	2.262	2.210

Orbitals energy (eV)

LUMO

2° excited state

1° excited state

HOMO

Compound 1: 26 σ^*_{S-S} 3.59; 212 nm; 219 nm; 25 n_{S1}, n_{S2} 9.53; 24 n_{S1}, n_{S2} 9.78; 23 σ_{S-S} 11.92; exp: 254 nm, $\varepsilon = 400^{13}$

Compound 2: 30 σ^*_{S-S} 2.72; 198 nm; 241 nm; 29 n_S 9.91; 28 $n_O - \sigma_{S-S}, n_S$ 10.57; 27 n_O 11.35; exp: 248 nm, $\varepsilon = 2300^{13}$

Compound 3: 34 σ^*_{S-S} 2.93; 150 nm; 218 nm; 33 n_S 10.8; 32 σ_{S-S}, n_O 11.75; exp: 236 nm, $\varepsilon = 72^{13}$

Compound 4: 34 σ^*_{S-S} 0.097; 248 nm ^{b}; 286 nm ^{b}; 33 σ_{S-S}, n_O 8.91; 32 n_S, n_O 11.32; 31 n_S, n_O 11.67; exp: 240-260 nm, $\varepsilon = 3000^{36b}$

Compound 5: 38 σ^*_{S-S} 1.80; 181 nm; 216 nm; 37 σ_{S-S}, n_O 10.44; 36 n_S, n_O 11.78; exp: 240-260 nm, $\varepsilon = 3000^{36b}$

Compound 6: 42 σ^*_{S-S} 2.65; 157 nm; 41 σ_{S-S}, n_O 11.40; exp: 215 nm, $\varepsilon = 3580^{42}$
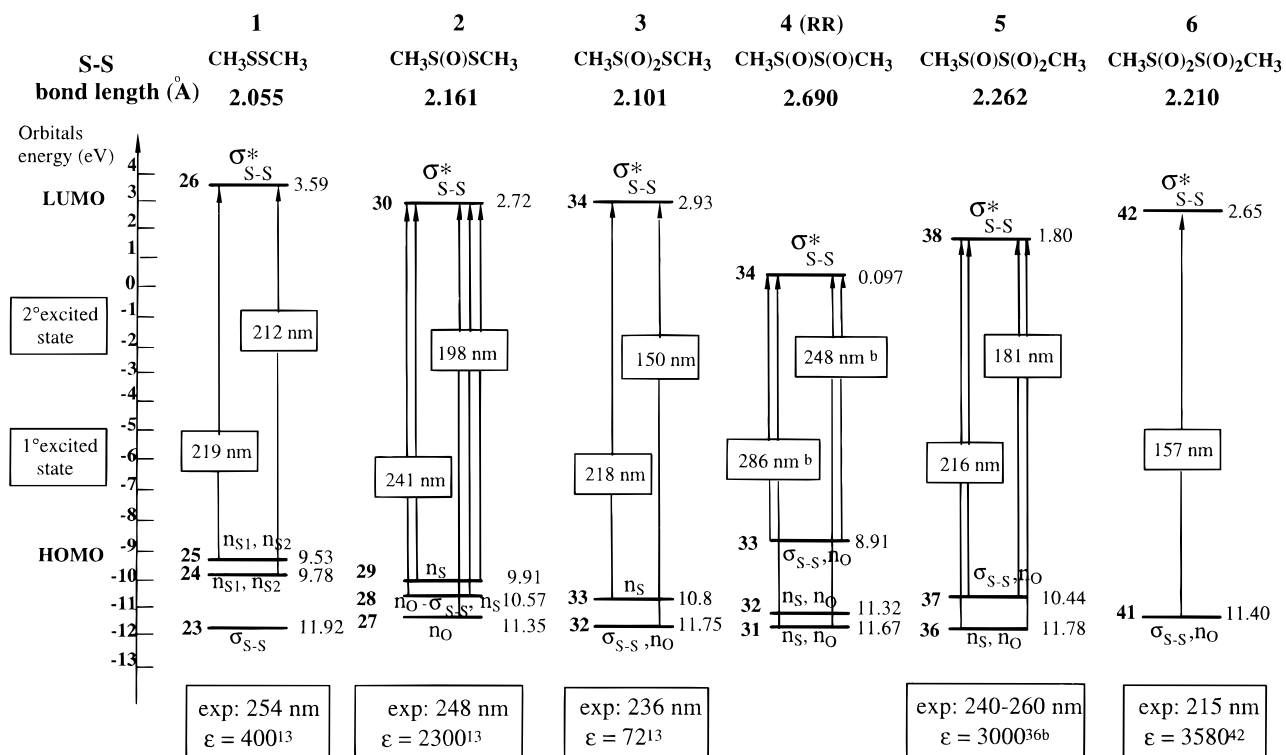
Figure 3. Simplified representation of the UV spectra of sulfur–sulfur-bridged isomers (see text for information). The calculated UV transitions, characterized by their wavelength (in nm) inside rectangles, are figured by arrows involving the most important single excited configurations. ^{b} As the first excited state is calculated with a null oscillator strength,[61] the second and third excited state are represented here.

for disulfoxide **4**, whereas this LUMO energy is found around 3 eV for disulfide **1** or thiosulfonate **3**. The low energy (2.65 eV) of the LUMO of disulfone **6** is also worthy of note.
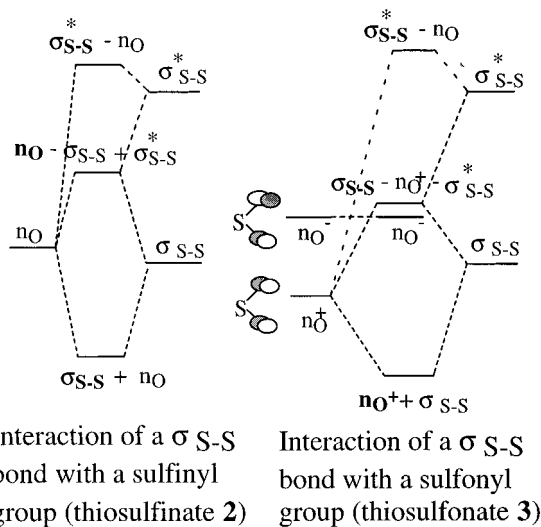
(b) The two highest occupied orbitals are always localized on sulfur (n_S) and oxygen (n_O) lone pairs, with a variable contribution of the σ_{S-S} bond. Once again, the energetic position of the orbital with a significant σ_{S-S} contribution is dependent on the presence of a sulfinyl group: its energy is -11.92 eV for disulfide **1** and -11.75 and -11.40 eV, respectively, for the sulfonyl derivatives **3** and **6**, while it is found at -10.57 eV for thiosulfinate **2**, -10.44 eV for sulfinyl sulfone **5**, and above all -8.91 eV for disulfoxide **4** with two sulfinyl functions.

(c) The decreasing order of the LUMO follows the increasing order of S–S bond lengths.

The main interactions are qualitatively depicted in Charts 1 and 2. The only considered interacting fragments are localized on the σ_{S-S} and σ^*_{S-S} orbitals and on the n_O lone pairs.

For thiosulfinate **2**, a strong first-order interaction between the σ_{S-S} bond and the oxygen lone pair n_O is completed by a second-order interaction with the σ^*_{S-S} bond, which accounts for the observed polarization of the S–S bond (Chart 1). For thiosulfonate **3**, the geminal oxygens lone pairs give two new bonding and antibonding combinations, respectively noted n_{O^+} and n_{O^-}. Only the in-phase n_{O^+} combination, stabilized relative to the oxygen lone pair of thiosulfinate **2**, can interact with the σ_{S-S} orbital. It thus follows weaker first-order (with σ_{S-S}) and second-order (with σ^*_{S-S}) interactions: the S–S bond is less polarized, and the weaker electronic transfer toward the σ^*_{S-S} orbital results in a shorter S–S bond.

Chart 1

Interaction of a σ_{S-S} bond with a sulfinyl group (thiosulfinate **2**)

$\sigma^*_{S-S} - n_O$
σ^*_{S-S}
$n_O - \sigma_{S-S} + \sigma^*_{S-S}$
n_O
σ_{S-S}
$\sigma_{S-S} + n_O$

Interaction of a σ_{S-S} bond with a sulfonyl group (thiosulfonate **3**)

$\sigma^*_{S-S} - n_O$
σ^*_{S-S}
$\sigma_{S-S} - n_O^+$
σ^*_{S-S}
n_O^-
n_O^+
σ_{S-S}
$n_O^{++} + \sigma_{S-S}$

These qualitative arguments are in line with the known enhanced experimental stability of **3** relative to **2**.

When two sulfinyl groups are present (disulfoxide **4**, Chart 2) the vicinal oxygen lone pairs form two combinations: the ($n_{O1} + n_{O2}$) one, symmetric (S) relative to the C_2 axis perpendicular to the S–S bond on one hand, and the antisymmetric (A) ($n_{O1} - n_{O2}$) one on the other hand. Significant first-order interactions are now possible: the first one between the symmetric σ_{S-S} orbital and the symmetric combination ($n_{O1} + n_{O2}$), resulting in a strongly destabilized ($\sigma_{S-S} - (n_{O1} + n_{O2})$) orbital, and the second one between the antisymmetric combination ($n_{O1} - n_{O2}$) and the antisymmetric σ^*_{S-S} orbital, resulting in

Chart 2
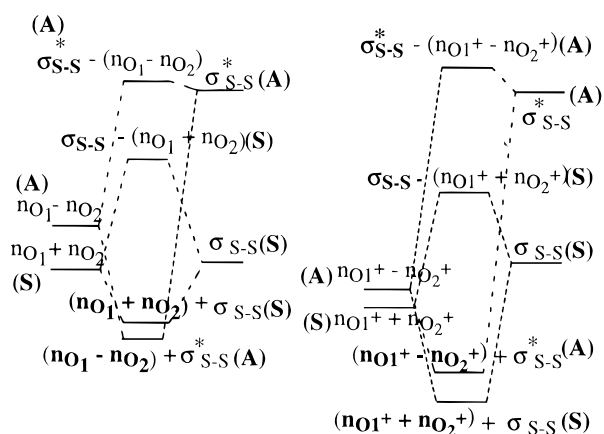
Interaction of a σ_{S-S} bond with two sulfinyl groups (disulfoxide **4**)

Interaction of a σ_{S-S} bond with two sulfonyl groups (disulfone **6**)

(A and S mean symetric or antisymmetric relative to a C_2 axis perpendicular to the S-S bond)

in a strongly stabilized $(n_{O1} - n_{O2} + \sigma^*_{S-S})$ orbital which is found lower in energy than the $(n_{O1} + n_{O2} + \sigma_{S-S})$ one.

The substantial lengthening of the S—S bond of **4**, like the low energetic position of the σ^*_{S-S} orbital, results from the large electronic transfer toward the σ^*_{S-S}. For the disulfonyl derivative **6**, only the n_{O^+} combination of the geminal oxygens can interact with the σ orbitals. They form the $(n_{O1^+} + n_{O2^+})$ (S) and $(n_{O1^+} - n_{O2^+})$ (A) combinations figured in Chart 2. For better clarity, the geminal n_{O^-} orbitals are not represented. These $(n_{O1^+} + n_{O2^+})$ and $(n_{O1^+} - n_{O2^+})$ orbitals are stabilized relative to the corresponding orbitals of disulfoxide **4**. A lower electronic transfer toward the σ^*_{S-S} orbital thus implies a conventional energetic position of the $(n_{O1^+} - n_{O2^+} + \sigma^*_{S-S})$ combination that is now found above the $(n_{O1^+} + n_{O2^+} + \sigma_{S-S})$ and a smaller S—S bond lengthening than for disulfoxide **4**. However, these first-order interactions are more significant than those depicted for thiosulfonate **3** and account for the longer bond length of disulfone **6** relative to thiosulfonate **3**.

A different situation prevails for sulfur—oxygen—sulfur-bridged derivatives (Figure 4). First, the σ_{S-O} orbital is found at a much lower energetic position than the σ_{S-S} orbital. Second, the energy of the LUMO is on the whole higher than previously thought: around 3.2 eV except for *O*-sulfinyl sulfonate **9** (2.85 eV). The LUMO is essentially localized on O—S sulfenyl single bond for sulfenyl derivatives **10**, **11**, and **7** and on the sulfinyl S(O)—O single bond otherwise (O-sulfinyl sulfonate **9** and sulfinic anhydride **8**). This in turn implies that S—O bond cleavage associated with an electronic transfer toward the σ^*_{S-O} orbital will only be possible for a sulfenyl (**10**, **11**) or a sulfinyl (**9**, **8**) bond but not for a sulfonyl bond. *OS*-Sulfenyl sulfinate **7** represents a particular case as its LUMO is located on the sulfenyl σ^*_{S2-O} bond with a contribution of the sulfinyl σ^*_{S1-O} bond: both S—O bond cleavage should thus be observed.

III. UV Spectra Evaluation with the CIS/6-31G* Method. With this method, the first excited states, i.e., UV transitions, are calculated through a simple config-

uration interaction scheme only involving single excited configurations: as a result, each excited state, associated with a transition characterized by its wavelength and oscillator strength (this latter one to be compared to the experimental molar extinction coefficient[58]), can be described by a linear combination of single excited configurations i→j where i and j represent the molecular orbitals involved in this configuration (detailed calculation results are available in the Supporting Information). A simplified representation of these results is given in Figures 3 and 4 for sulfur—sulfur- and sulfur—oxygen—sulfur-bridged compounds, respectively: in these Figures, the energetic positions of the most important orbitals are given (in eV) together with their nature and their numbering in bold characters.

It is worth recalling the experimental UV spectra[13] of dimethyl disulfide (**1**), methyl methanethiosulfinate (**2**), and methyl methanethiosulfonate (**3**). In acetonitrile solutions, these compounds exhibit their maximum UV absorption at 254, 252 (260 in the gas phase) and 236 nm, respectively, but with very different molar extinction coefficients: 400 L·mol^{-1}·cm^{-1} for **1**, 2300 L·mol^{-1}·cm^{-1} for **2**, and 72 L·mol^{-1}·cm^{-1} for **3**. For methyl methanethiosulfinate (**2**), despite an accurate examination of its UV spectrum, we could not find out the weak intensity band ($\epsilon = 10$ L·mol^{-1}·cm^{-1}) at 320 nm previously reported.[41,42] Some data have also been collected for sulfinyl sulfone **5** and isomeric sulfinic anhydride **8**:[36b] the UV spectrum of **5** presents a broad shoulder from about 240−260 nm ($\epsilon \cong 3000$ L·mol^{-1}·cm^{-1}), while 2-methyl-2-propane-sulfinic anhydride (**8a**) (R = *t*-Bu) is characterized by λ_{max} 238 nm, $\epsilon = 2300$ L·mol^{-1}·cm^{-1}. The UV spectrum of dimethyl disulfone **6** shows an intense band ($\epsilon = 3580$ L·mol^{-1}·cm^{-1}) at short wavelength (215 nm).[42]

Before describing the calculated UV transitions, it should be born in mind that these results are only valid for long-wavelength transitions, i.e., above 200 nm, since it is known that Rydberg excited states are likely to occur under this threshold.[59] Accordingly, only the first transitions (one to three) expected to be observed above 200 nm are descibed in the following. We checked only for thiosulfinate **2**, from its gas-phase UV spectrum, which is not strikingly different from its solution spectrum, that no Rydberg transitions occur between 200 and 250 nm. From Figure 3, it immediately appears that the calculated CIS/6-31G* wavelengths are always underestimated by about 40 nm. Previous calculations of the UV spectra of HSSH and CH$_3$SSCH$_3$ also gave underestimated wavelengths by about 40 nm.[60] More accurate wavelengths are only obtained with a more extensive configuration interaction (vide infra).

Examination of Figure 3 makes it evident that the two first excited states for these sulfur—sulfur-bridged molecules are described by single excited configurations where the LUMO σ^*_{S-S} is always involved and that have

(58) The oscillator strength *f* is proportional to the integrated intensity of the absorption band $f = 4.319 \times 10^{-9} \int \epsilon d\nu$ (with ν as the average wavenumber of the absorption band in cm^{-1} and ϵ as the molar extinction coefficient in L·mol^{-1}·cm^{-1}). It is related to the theoretically determinable dipolar transition moment M_{0k} for an electric dipolar transition between the ground state ψ_0 and the excited state ψ_k: $M_{0k} = \langle \psi_0 | \mu | \psi_k \rangle$ (with μ as the operator of the electric dipolar moment) and $f_{ok} = |M_{0k}|^2 8\pi^2 m c \nu_{ok}/3he^2 = 4.073 \times 10^{29} \nu_{ok} |M_{0k}|^2$). From *The theory of the Electronic Spectra of Organic Molecules*; Murrel, J. N., Ed.; Methuen and Co.: London, 1963; pp 6−9.

(59) In *Higher Excited States of polyatomic molecules*; Robin, M. B., Ed.; Academic Press: New York and London, 1974; Vol. 1.

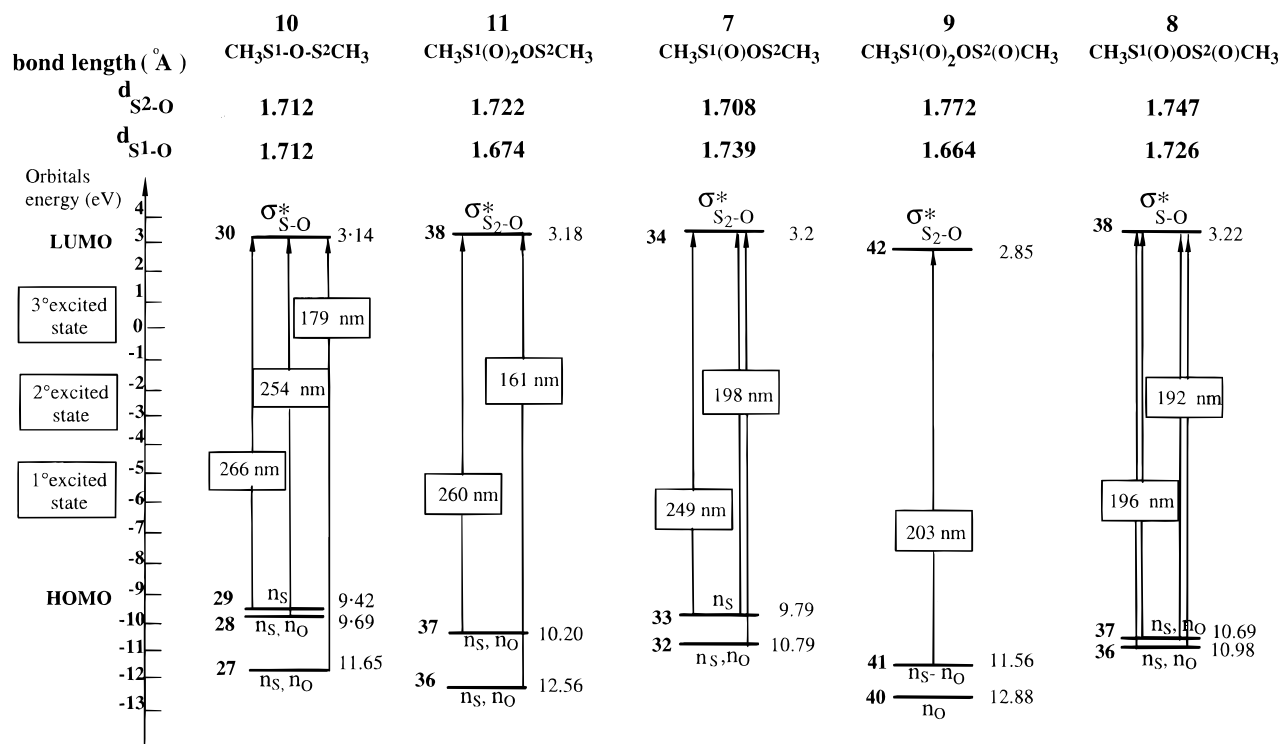(60) Rauk, A. *J. Am. Chem. Soc.* **1984**, *106*, 6517−6524.

Figure 4. Simplified representation of the UV spectra of sulfur−oxygen-bridged isomers (see text for information). The calculated UV transitions, characterized by their wavelength (in nm) inside rectangles, are figured by arrows involving the most important single excited configurations.

an important coefficient. If it is assumed for disulfide **1** and thiosulfinate **2** that the experimental broad band most probably includes the two first excited states, the order of calculated oscillator strengths (0.0115 and 0.0003 for **1**, 0.0068 and 0.1006 for **2**) accounts for the increase in molar extinction coefficient from **1** (ϵ = 400 L·mol^{-1}·cm^{-1}) to **2** (ϵ = 2300 L·mol^{-1}·cm^{-1}). For thiosulfonate **3**, the oscillator strength of the sole intervening first state (0.0006) is the smallest of the family, in good agreement with experimental order of molar extinction coefficients (ϵ = 72 L·mol^{-1}·cm^{-1}). Among stable molecules **1−3**, the greatest oscillator strength is thus obtained for the second excited state of **2** where a $\sigma_{S-S} \rightarrow s^*_{S-S}$ transition (**28 → 30**) has an important coefficient.

This comparison between experimental and theoretical data thus implies that accurate absorption wavelengths are not to be obtained by this method but that the nature and the intensity of the UV transitions may be compared within a family.

A high photochemical reactivity is expected for **4**, with a long wavelength absorption deduced from the high and low energy of the HOMO and of the LUMO, respectively. Moreover, the $\sigma_{S-S} \rightarrow s^*_{S-S}$ (**33→34**) transition appears with an important coefficient in the second and third excited states (the first one is calculated with a null

oscillator strength[61]). It is symmetry favored and explains the strong oscillator strengths (0.2661 and 0.6122) associated with these two states for this molecule with a C_2 symmetry.

To a lesser extent, the same observations hold true for sulfinyl sulfone **5**: an important oscillator strength is calculated for both first states (0.1599 and 0.244) because of the weight of the $\sigma_{S-S} \rightarrow \sigma^*_{S-S}$ (**37→38**) configuration. However, here, the absorption wavelength is calculated in the same area as for disulfide **1**, thiosulfinate **2**, or thiosulfonate **3**. These estimations are quite consistent with the previously mentioned experimental spectrum of **5**[36a] (λ between 240 and 260 nm, ϵ = 3000 L·mol^{-1}·cm^{-1}).

The characteristics of the first excited state of disulfone **6** are easily understood in light of the nature of the sole intervening configuration ($\sigma_{S-S} \rightarrow \sigma^*_{S-S}$, i.e., **41 → 42**) and of the energy of the σ_{S-S} HOMO and σ^*_{S-S} LUMO: strong oscillator strength (0.755) and small absorption wavelength in excellent agreement with the experimental spectrum[42] (λ = 215 nm, ϵ = 3580 L·mol^{-1}·cm^{-1}).

For the three S−O−S-bridged sulfenyl derivatives **10**, **11**, and **7** (Figure 4), one or two long wavelength first excited states are calculated (around 250 nm). Taking into account the previously observed underestimation of wavelengths, the UV absorption of these compounds would thus probably begin around 300 nm. For the sulfinyl derivatives **9** and **8**, the absorption maximum should be close to that of the sulfur−sulfur-bridged isomers **1**, **2**, or **3**. The only available experimental data are relative to sulfinic anhydride **8a** (λ_{max} 238 nm, ϵ = 2300 L·mol^{-1}·cm^{-1})[36b] and support our evaluation.

IV. Calculation of the UV and Photoelectron Spectra of Methyl Methanethiosulfinate (2) by an Extensive Configuration Interaction Method. To obtain a more accurate estimation of absorption wave-

(61) Disulfoxide **4RR** belongs to the C_2 symmetry group. Accordingly, the transition probability will be different from zero if the direct product of the irreducible representation $\Gamma_0 * \Gamma_\mu * \Gamma_k$ contains the totally symmetric representation (with Γ_0 as the irreducible representation associated with the ground state of A symmetry, Γ_k as the irreducible representation associated with the excited state, and Γ_μ as the irreducible representation associated with the operator of the electric dipole moment). The sole transition moments different from zero are found with B symmetry. They will give nonnull oscillator strength f when operating on B symmetry excited states, i.e., **32 → 34** and **31 → 34**, since **33 → 34** is of A symmetry.

Table 6. Comparison between the Calculated and Experimental First UV Transitions (in nm) of Methyl Methanethiosulfinate (2) within the MRSDCI/6-31G* Formalism

	ground state	1° excited state	2° excited state	3° excited state	4° excited state	5° excited state
calcd transition (nm) and oscillator strength f		304.7 $f = 0.003\ 34$	261.1 $f = 0.030\ 89$	227.0 $f = 0.007\ 85$	222.0 $f = 0.097\ 23$	200.0 $f = 0.097\ 99$
exptl transition (nm)		between 230 and 300 (max at 252 in CH_3CN, 260 in the gas phase) $\epsilon = 2300$ L·mol^{-1}·cm^{-1} in solution				

length, a more extensive configuration interaction is necessary. The results obtained with the method described in the Computational Methods section for the model molecule methyl methanethiosulfinate (**2**) in its MP2/6-31G*-optimized geometry are given in Table 6.

The five first excited states are now described by numerous configurations (not only single excited ones) among which the previously mentioned single excited configurations have the most important coefficient: **29 → 30** for the first excited state and **28 → 30** for the second, while the third one involves orbitals next to the LUMO (**29 → 31** and **28 → 31**). The fourth and fifth excited states have significant coefficients on the **27 → 30** and **28 → 31** configurations, respectively. We are accordingly dealing with the same first excited states as previously calculated within the CIS/6-31G* formalism. From the calculated wavelengths of the four first excited states (between 305 and 222 nm) and from the weak oscillator strengths of the first excited state, our initial assumption still holds true: the broad experimental band between 300 and 230 nm with a maximum at 252 nm in solution and 260 nm in the gas phase probably not only includes the first two excited states but rather the four first ones, accounting for the high molar extinction coefficient. The fifth state should be observed at shortest wavelengths as it is calculated at 200 nm: it probably partly corresponds to the short wavelength (around 200 nm in the gas-phase spectrum) intense experimental band. The calculated wavelengths with this extensive configuration interaction treatment thus much better fit the experimental data.

Another test to assess the accuracy of these calculations refers to ionization potential (IPs) estimation, which can be compared to experimental IPs in the case of **2**.[43] The photoelectron spectrum has been described with three first bands at 9.12, 9.51, and 10.38 eV. From Helium II experiments, it was concluded that the two first bands arise from the ejection of an electron from orbitals heavily localized on sulfur, while the third band is concerned with the ejection of an electron from an orbital more heavily localized on oxygen. The orbitals description of **2** in Figure 3 is in good agreement with these experimental observations. However, as is usual for these heteroatomic molecules,[43] Koopman's evaluation, i.e., IP $= -\epsilon_i$ where ϵ_i refers to the energy of orbital i, gives overestimated IPs (Figure 3): 9.91 against 9.12 eV for the first IP, 10.57 against 9.51 eV for the second one, and 11.35 against 10.38 eV for the third one. The poor accuracy of the UV wavelength evaluation within the CIS/6-31G* methodology is accordingly easily understood. On the other hand, vertical IPs calculation within the configuration interaction treatment gives good results at this approximation level (Table 7): 9.00, 9.61, and 10.14 eV.

This calculation method thus provides more reliable and accurate estimation of photoelectron and UV spectra than the MP2 or CIS/6-31G* formalism. However, this

Table 7. Comparison between the Calculated and Experimental Three First Ionization Potentials (in eV) of Methyl Methanethiosulfinate (2) within the MRSDCI/6-31G* Formalism

	1° ionic state	2° ionic state	3° ionic state
calcd IPs (eV)	9.00	9.61	10.14
exptl IPs (eV)[43]	9.12	9.51	10.38

more precise method is also much more expensive and time-consuming. Its use for the whole set of molecules presented in this work was not conceivable. Moreover, the combined MP2-CIS/6-31G* method allows a good understanding of their electronic properties and the comparison of the spectra of these molecules within a series appears to give consistent results.

Discussion

This analysis allows a first estimation of the stability and of the photochemical reactivity of the studied compounds. For sulfur−sulfur-bridged molecules **2**−**6**, the important results concern the length of S−S bonds on one hand and the nature of their first UV absorption, which is always associated with a $\sigma_{S-S} \rightarrow \sigma^*_{S-S}$ transition, on the other hand. Accordingly, these oxysulfur molecules will easily lead thermally, but above all photochemically, as observed in numerous experiments, to radicals arising from S−S bond cleavage[12−14,18−27] (eq 2). The S−S bond appears to be particularly weak when a sulfinyl group is present in the molecule. Taking into account the unpaired electron spin distribution in either sulfinyl (59% on sulfur, 41% on oxygen)[62] or sulfonyl radicals (42% on sulfur, 44% on oxygens),[63] their coupling through the sulfur−oxygen or sulfur−sulfur bond could actually occur. They thus give rise to sulfur−oxygen-bridged isomers,[22,26,27,32] the energies of which are not inconsistent with this observation (Table 3). In fact, the sulfur−oxygen-bridged isomers are calculated to be the thermodynamical coupling products between two sulfinyl radicals (**7**), between two sulfonyl radicals (**9**), or between a sulfinyl and a sulfonyl radical (**11**).

For these O−S-bridged molecules, once again long S−O bond lengths have been calculated for compounds with a sulfenyl or a sulfinyl moiety, while S−O bond lengths of sulfonate functions are shorter. The first UV absorptions for these derivatives are associated with $n_S, n_O \rightarrow \sigma^*_{S-O}$ transitions and involve sulfenyl and sulfinyl bond breaking, whereas sulfonate bonds should not be photochemically cleaved. *OS*-Sulfenyl sulfinate **7**, with both a sulfenyl and a sulfinyl moiety, should be prone thermally (owing to the long S−O bond lengths), or photochemically,

(62) Swarts, S. G.; Becker, D.; DeBolt, S.; Sevilla, M. D. *J. Phys. Chem.* **1989**, *93*, 155−161.
(63) Chatgilialoglu, C.; Griller, D.; Guerra, M. *J. Phys. Chem.* **1987**, *91*, 3747−3750.
(64) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3921−3929.
(65) Benson, C. W. *Chem. Rev.* **1978**, *78*, 23−55.
(66) Lee, J. D.; Bryant, M. W. R. *Acta Crystallogr.* **1969**, *25B*, 2094−2096.

to either S−O bond breaking and should lead either to a thiyl CH$_3$S$^\bullet$ and a sulfonyl CH$_3$SO$_2^\bullet$ radical or to two sulfinyl radicals CH$_3$SO$^\bullet$, accounting for numerous experimental observations[12–14,37] and eqs 1−3.

On the contrary, *OS*-sulfenyl sulfonate **11** should give upon irradiation only thiyl CH$_3$S$^\bullet$ and sulfonyloxyl CH$_3$SO$_2$O$^\bullet$ radicals by sulfenyl bond breaking while *O*-sulfinyl

$$CH_3S(O)_2OSCH_3 \xrightarrow{\ h\nu\ } CH_3SO_3^{\bullet} + CH_3S^{\bullet} \qquad (7)$$
$$\mathbf{11}$$
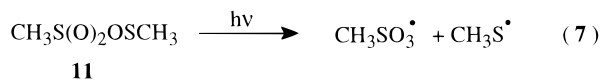
sulfonate **9** should only give sulfinyl CH$_3$SO$^\bullet$ and sulfonyloxyl CH$_3$SO$_3^\bullet$ radicals by sulfinyl bond cleavage

$$CH_3S(O)_2OS(O)CH_3 \xrightarrow{\ h\nu\ } CH_3SO_3^{\bullet} + CH_3SO^{\bullet} \qquad (8)$$
$$\mathbf{9}$$
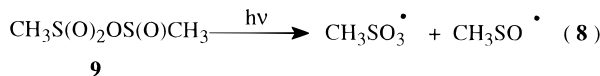
These results are in agreement with all the available experimental data for *O*-sulfinyl sulfonate **9**[22,13,30–34] and for some of them in the case of photochemical reactions involving *OS*-sulfenyl sulfonate **11**.[30] However, in the RS$_2$O$_3$R series, the possible formation of sulfinic anhydride **8**, accounting for the experimentally observed formation of sulfinic acid RSO$_2$H,[13,30] cannot be ruled out.

To summarize, sulfur−oxygen-bridged isomers **7**, **9**, **11**, and alternatively **8** are essential to explain the experimentally observed disproportionation of oxysulfur radicals. They are calculated to be rather stable compounds, either slightly less stable (**10** and **7**) or even more stable (**11**, **8**, and **9**) than their sulfur−sulfur-bridged isomers. However, they are hardly observed experimentally. This is probably due to a short lifetime, as these compounds should be cleaved very easily into radicals either thermally (long sulfinyl or sulfenyl S−O bond lengths) or photochemically. Moreover, these derivatives should be very sensitive to hydrolysis and give rise to the corresponding sulfenic RSOH, sulfinic RSO$_2$H, or sulfonic RSO$_3$H acids. In other words, they probably can be considered as stable species relative to their sulfur−sulfur-bridged isomers, but they should readily undergo further reactions leading either to oxysulfur radicals or to oxysulfur acids in hydrolytic media. Their isolation should, however, be possible under carefully controlled conditions.

Conclusion

This theoretical study provides geometrical, energetic and spectroscopic data on oxysulfur compounds derived from dimethyl disulfide, improving the understanding of some important features which prevail in the experimental behavior of these derivatives.

From a geometrical point of view, the S−S bond lengths of sulfur−sulfur-bridged isomers and the sulfenyl and

sulfinyl S−O bond lengths of sulfur−oxygen-bridged derivatives are calculated to be rather long, evidencing weak S−S or S−O bonds. An interesting result was obtained for dimethyl disulfoxide **4**, as its most stable *RR* diastereoisomer was calculated with the longest S−S bonds (2.69 and 2.744 Å for the two different conformers): the latter conformer is similar to a cyclic adduct **12a** between two sulfinyl radicals and is also calculated as the optimized geometry of the disulfenic peroxide **13a**, nicely accounting for Clennan results relative to singlet oxygen addition on disulfides[28] (eq 3).

The first UV absorptions for these oxysulfur molecules are always associated with $\sigma_{S-S} \rightarrow \sigma^*_{S-S}$ transitions for sulfur−sulfur-bridged molecules or with $n_S, n_O \rightarrow \sigma^*_{S-O}$ transitions for sulfur−oxygen-bridged isomers. Accordingly, under irradiation, S−S bond breaking in the former case and sulfenyl and/or sulfinyl S−O bond breaking in the latter will be observed. As a result, the photochemical reactivity of these derivatives will be very similar to their thermal reactivity, with radicals formation by S−S or S−O bond cleavage. These observations are in agreement with all the experimental data. They are also consistent with various studies dealing with sulfinyl and sulfonyl coupling/disproportionation reactions.

This study also demonstrates that standard ab initio methods can give a good estimation of the UV spectra in this series of molecules: even if the calculated wavelengths are not accurate, their evolution within this family and moreover the comparative evaluation of the molar extinction coefficients appear to be quite reliable.

Supporting Information Available: Table 1 (geometrical parameters of dimethyl disulfide **1**, methyl methanethiosulfinate **2**, and dimethyl sulfenic anhydride **10**), Table 2 (geometrical parameters of CH$_3$S$_2$O$_2$CH$_3$ isomers: methyl methanethiosulfonate **3**, disulfoxide **4**, *OS*-sulfenyl sulfonate **7**), Table 3 (geometrical parameters of CH$_3$S$_2$O$_3$CH$_3$ isomers: sulfinyl sulfone **5**, sulfinic anhydride **8**, *OS*-sulfenyl sulfonate **11**), Table 4 (geometrical parameters of CH$_3$S$_2$O$_4$CH$_3$ isomers: disulfone **6** and *O*-sulfinyl sulfonate **9**), Table 5 (MP2/6-31G* energies of compounds **1**−**11**), Table 6 (calculated wavelengths for the first excited states of sulfur−sulfur-bridged compounds **1**−**6**), Table 7 (calculated wavelengths for the first excited states of sulfur−oxygen-bridged compounds **10**, **11**, **7**, **9**, and **8**), Table 8 (energies (in hartrees) of the ground state and five first excited states of methyl methanethiosulfinate **2** within the MRSDCI/6-31G* formalism), Table 9 (energies (in hartrees) of the ground state and three first ionic states of methyl methanethiosulfinate **2** within the MRSDCI/6-31G* formalism), and Table 10 (*Z*-matrices of all stationary points) (16 pages). The material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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