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Density Functional Theory Study of the Dimerization of the Sulfine H_2CSO

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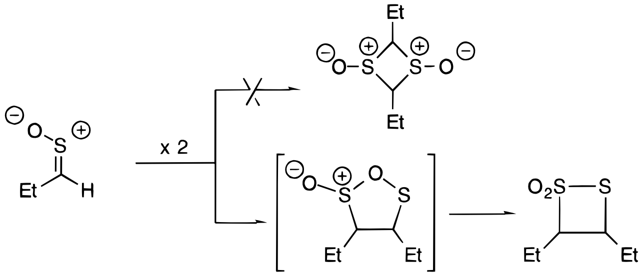
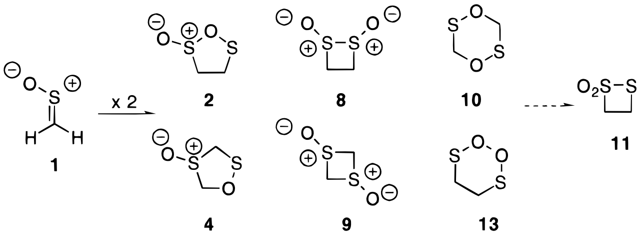
The dimerization mechanism of the sulfine H_2CSO (**1**) is studied using a hybrid DFT method (B3LYP) with a large basis set on the sulfur atom. Single-points post-HF calculations up to the CCSD(T) level were performed for some representative stationary points of the potential energy surface. The (2 + 3) mechanism was predicted to be the lowest energy pathway, with an activation barrier of 12.3 kcal/mol; the bond formation process is very asynchronous (in the first stage of the reaction, the C−C bond formation is more advanced than the S−O one) and probably a stepwise mechanism occurs involving a biradical intermediate. The alternative pathway involving an anti transition structure occurs with an activation energy equal to 13.7 kcal/mol and is slightly less favorable. In both cases, the obtained cycloadduct is the five-membered ring **2**. Concerted ($2_s + 2_a$) or (3 + 3) pathways necessitate larger activation energies (≅33 kcal/mol). Despite an extensive search, we were unable to find a reaction path for the rearrangement of **2** to the more stable four-membered adduct **11**, which is the expected final term of the dimerization reaction.

In contrast with sufines derived from ketones,[1] which are generally stable compounds, simple aldehydic sulfines (thioaldehyde *S*-oxides) are relatively unstable and cannot survive for a long time on the bench at room temperature.[2] Probably the most famous sulfine is propanethial *S*-oxide (Scheme 1), the lachrymatory factor of onion.[3] It was first proposed that this compound dimerizes into a symmetrical (2 + 2) cycloadduct.[4] However, Block and his team[3,5] reexamined this problem and proposed that the right dimer structure is that of a cyclic thiosulfonate. This structure, which is now well-accepted, would result from a 1,3-dipolar cycloaddition, giving a five-membered ring intermediate, which would then rearrange to the final product. Although it looks reasonable, no definitive evidence has been given for the proposed mechanism.[6] A similar structure has been described for the dimer of (trimethylsilyl)methanethial *S*-oxide.[7]

Scheme 1



Scheme 2[a]



[a] The numbering presented has been chosen for the sake of clarity of the following discussions and figures.

Here we present our results concerning the possible cyclization products of the prototypal sulfine methanethial *S*-oxide (**1**). Our goal is to clarify the question of the mechanism leading from a sulfine to its dimer using theoretical calculations. In particular, such calculations would inform us about which major primary adduct could be obtain. In principle, six dimers can be formed from **1** (Scheme 2). The five-membered rings **2** and **4** would be formed by 1,3-dipolar cycloadditions. The four-membered rings **8** and **9** would result from head-to-head and head-to-tail (2 + 2) cycloadditions. In the case of **10** and **13** (3 + 3) cycloadditions would be involved.

Ab initio studies of hypervalent sulfur-containing molecules are notoriously difficult and sometimes show large basis set effects.[8] Particularly, Burgers and coworkers found that standard G1 and G2 calculations did not provide accurate heat of formation because of the inadequate basis set (6-31G(d)) that was used for geom-

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[6] However, sulfines are known to take part in 1,3-dipolar cycloadditions. The sulfine can act as the dipolarophile (Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Thijs, L.; Veenstra, G. E.; Zwanenburg, B. *J. Chem. Soc., Perkin Trans 1* **1978**, 1218) or as the dipole (Huisgens, R.; Mloston, G.; Polborn, K. *J. Org. Chem.* **1996**, *61*, 6570).

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10.1021/jo9823543 CCC: $18.00

etry optimizations.[9] These authors have shown that larger split-valence basis sets, e.g. 6-311+G(2df,2p), were required to obtain reliable equilibrium structures. In addition, uncorrelated geometries using large basis sets fail to reproduce experimental trends (vide infra).

In the last years, much interest has been devoted to methods rooted in the density functional theory (DFT),[10] which are at the heart of a convenient computational approach capable of describing successfully problems previously covered exclusively by post-HF methods. DFT methods scale only with the ca. 3 power of the number of basis set functions and thus allows one to use a larger basis set for geometry optimizations. In this work, to elucidate the mechanistic details for this dimerization, we use Becke's hybrid functional (B3LYP).[11] This functional has been used to describe sulfur derivatives containing nonconventional sulfur−oxygen double bond.[12] In addition, the B3LYP approach has already been shown to be useful to describe transition states (TSs) of cycloaddition reactions, even if the DFT wave function suffers from spin contamination.[13] Thus, by construction of the functional, DFT is capable of accurately representing systems that, at the molecular orbital level of theory, would otherwise require accounting for dynamical and/or nondynamical correlation effects.

Calculations

Calculations were performed using the Gaussian 94 suite of programs;[14] structural features (geometry optimizations, vibrational frequency, and IRCs) have been obtained with B3LYP using the 6-31+G(d,p) basis set[15] extended with two d-type functions and one f-type function on S atoms (hereafter referred to as 6-31+G(d,p),S(3df)). Basis set effects on relative energies have been tested by B3LYP/6-311+G(3df,2p) single-point calculations. Transitions structures have been confirmed by frequency calculations, and in the majority of cases, the corresponding two minima have been established by tracing the IRC.

Table 1. Geometries and Dipole Moment (μ) of Sulfine 1 at Various Levels of Calculation

level of calculation	S−O (Å)	S−C (Å)	OSC (deg)	μ (D)
HF/6-31+G(d,p)	1.462	1.587	114.6	4.03
HF/6-311+G(d,p)	1.456	1.585	114.6	4.09
HF/6-311+G(2df,2p)	1.439	1.579	115.2	3.59
HF/6-311+G(3df,2p)	1.433	1.576	115.5	3.50
B3LYP/6-31+G(d,p)	1.498	1.625	115.1	3.12
B3LYP/6-311+G(2df,2p)	1.479	1.611	114.9	3.19
B3LYP/6-311+G(3df,2p)	1.472	1.607	115.2	3.11
B3LYP/6-31+G(d,p),S(3df)	1.480	1.614	115.0	3.23
MP2/6-31+G(d,p)	1.501	1.630	114.6	4.39
MP2/6-311+G(2df,2p)[a]	1.476	1.616	115.3	
QCISD/6-31+G(d,p)	1.510	1.626	113.2	4.41
CASSCF/DZ (2df,2d,p)[a]	1.475	1.607	116.2	
experimental[b]	**1.469**	**1.610**	**114.7**	**2.99**

[a] From ref 9. [b] From ref 19.

Restricted B3LYP (RB) was used for closed-shell species, and the stability of the corresponding wave function for concerted transition structures has been tested. Unrestricted B3LYP (UB) calculations were carried out for diradicaloid species. Total spin expectation values $\langle S^2 \rangle$ for Slater determinants formed from the unrestricted Kohn−Sham orbitals were on the order of 0.9 for the broken-spin-symmetry singlets.

The electronic structures of the various stationnary points were analyzed by the natural bond orbital (NBO) method[16] employing the program G94NBO.[17]

Results and Discussion

Sulfine − Choice of Basis Set. Sulfine **1** can be written either in a neutral or dipolar form and will in reality contain components of both resonance structures:

$$H_2C{=}S{=}O \leftrightarrow H_2C{=}S^+{-}O^-$$

The known chemistry of **1** and its electronic structure are consistent with the dominance of the dipolar form (for example, the protonation occurs on the O atom[18] and NBO analysis indicates that the best Lewis structure is the dipolar one). As mentionned in the Introduction, the geometrical structure of sulfine **1** strongly depends on the basis set used in the calculation. The geometrical parameters and dipole moment obtained at various levels of theory are summarized in Table 1.

It appears that S−O and S−C bond lengths are more sensitive than the OSC bond angle to the level of theory. At the HF level, the disagreement between calculated and experimental sulfine geometry increases with the increase of the basis set. The opposite trend is observed when electron correlation is taken into account; the best agreement with experimental results is achevied when one puts f function on heavy atoms. It is noteworthy that the geometry calculated at the B3LYP/6-311+G(3df,2p) level is very close to the experimental one. However, the more economical 6-31+G(d,p)S(3df) basis set provides satisfactory geometry and dipole moment and was used for B3LYP geometry optimizations.

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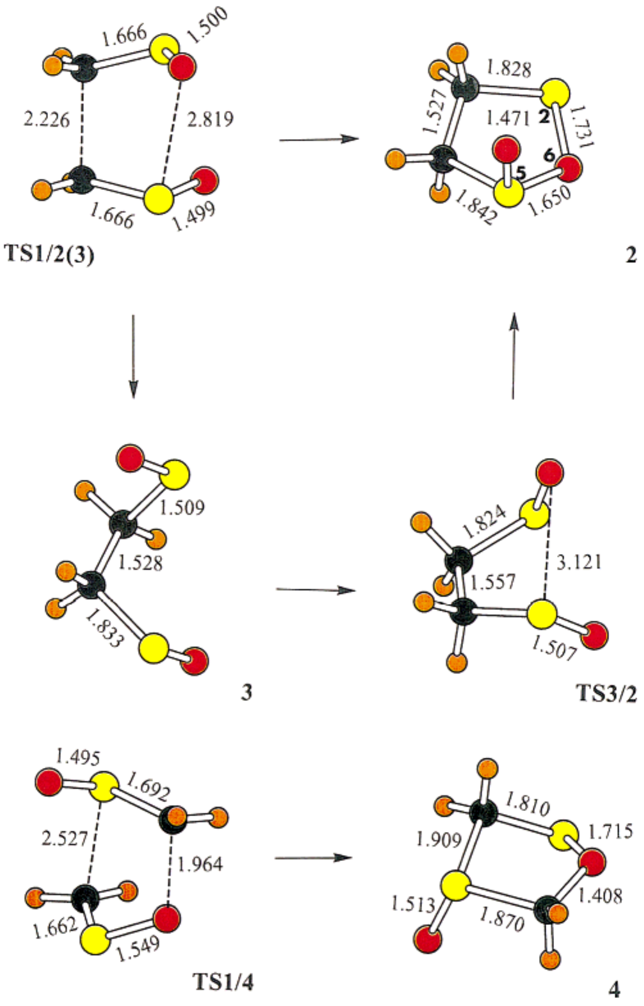

Figure 1. Summary of the (3 + 2) reaction pathways and selected geometric parameters for relevant species optimized at the B3LYP:6-31+G(d,p),S(3df) level.

Table 2. Relatives Electronic Energies (Δ*E*), Zero Point Energy Correction [Δ(ZPE)], Enthalpies (Δ*H*) (298.15 K), and Entropies (Δ*S*) (298.15 K) for the (2 + 3) Cycloaddition Reaction[a]

molecule	$\Delta E^{b,d}$	$\Delta(\mathrm{ZPE})^{b}$	$\Delta H^{b,d}$	ΔS^{c}
1 (H_2CSO)	0.0	0.0	0.0	0.0
TS1/2	10.4 (11.4)	1.6	11.3 (12.3)	−36.1
2	−27.6 (−25.7)	4.7	−24.1 (−22.2)	−45.6
3	−15.5 (−13.3)	3.1	−15.5 (−13.3)	−36.2
TS3/2	−10.5 (−8.2)	3.0	−12.6 (−10.4)	−41.7
TS1/4	16.1 (17.3)	1.6	17.0 (18.2)	−42.9
4	−15.2 (−12.5)	4.4	−12.0 (−9.3)	−45.5

[a] For the reference system **1**, the total energy (hartrees) is −1025.383 87 (6-31+G(d,p),S(3df)) or −1025.506 17 (6-311+G-(3df,2p)); the ZPE and temperature correction (hartrees) are 0.05810 and 0.00886, respectively, and the entropy is equal to 124.9 e.u. [b] In kcal/mol. [c] In cal/mol/K. [d] Values in parentheses correspond to single point 6-311+G(3df,2p)//6-31+G(d,p),S(3df) calculations.

(2 + 3) Cycloaddition ((1 − 3)-Dipolar Cycloaddition). Basically, two possible mechanisms exist for dipolar cycloaddition reactions: the concerted and the diradical stepwise pathways. To investigate the presence of any possible biradicaloid electronic structure in the transitions states, the optimizations were repeated with the UB method. The optimized structures of the stationary points corresponding to the head to head (2 + 3) cycloaddition are shown in Figure 1; their relative energies are given in Table 2.

A highly asynchronous structure is located for **TS1/2(3):** natural localized molecular orbitals/natural population analysis (NLMO/NPA) bond orders ($n_{\mathrm{CC}} = 0.232$, $n_{\mathrm{SO}} = 0.048$) confirm that the formation of the C−C bond is more advanced than the formation of the S−O one. This transition structure is not UHF unstable. Using the RB method, IRC calculations indicate that **TS1/2(3)** is connected to the cycloadduct **2**. However, this concerted reaction path is found very asynchronous: for instance, for a value of the reaction coordinate $s = -3.0$, $d_{\mathrm{CC}} = 1.659$ Å and $d_{\mathrm{SO}} = 2.744$ Å; for $s = -6.0$, $d_{\mathrm{CC}} = 1.556$ Å and $d_{\mathrm{SO}} = 2.491$ Å; thus, the C−C bond-making process occurs first. This very asynchronous formation of the new bonds suggests the possibility of a stepwise process involving a diradical singlet intermediate. But, such an intermediate cannot be described by restricted RB3LYP calculations; unrestricted UB3LYP calculations were required to obtain the diradical intermediate **3**. To find a reaction path from **1** to **3**, we tried to locate an UB3LYP TS; all our attemps led to the same transition structure that was found by the RB3LYP calculations (i.e., **TS1/2**). Thus, in this part of the potential surface, the singlet UB3LYP initial guess converges to an $S^2 = 0$ RB3LYP solution. It is only in regions of the potential surface beyond **TS1/2** that UB3LYP calculations give a lower energy than RB3LYP calculations, and UB3LYP IRC confirms that this TS is connected to diradical **3**. Then, a rotation around the C−C bond leads to **2** via **TS3/2** (see Figure 1). Our results predict that this cycloaddition can occur by two different types of pathways which diverge only after passage via a common transition state. Because the wave function for DFT calculations is a single determinant of Kohn−Sham orbitals, CASPT2 calculations, which provide a balanced treatment of concerted and diradical mechanism, should be considered in order to conclude on the nature of **TS1/2(3)** and on the existence of two different pathways. It should be noticed, however, that similar results were obtained by Borden and co-workers in their study at both (U)B3LYP and CASPT2 levels on the Cope rearrangement of 1,2,6-heptatriene.[20] **TS1/2(3)** lies 10.4 kcal/mol above the reactants while **TS3/2** is 10.5 kcal/mol below the reactants. The resulting five-membered ring **2** is calculated to be 27.6 kcal/mol more stable than the two isolated sulfine molecules. One can notice that the C=S double bond in the $H_2C{=}S{-}H_2C{=}N^{+}(O)^{-}H$ system is more reactive, the (1 − 3) cycloaddition occurring with an energy barrier of only 2.5 kcal/mol.[21] The use of the larger basis set produces an increase of all relative energies by 1.0−2.3 kcal/mol, which would be tentatively attributed to a lesser basis set superposition error (BSSE). The inclusion of zero-points and thermal corrections to the energy, as well as the entropy, does not change fundamentally the relative order given by potential energies. Another point concerning energetic aspects is the spin-contamination of the diradicaloid structures. As mentionned in the calculation part, $\langle S^2\rangle$ values for diradicaloid structures are in the order of 0.9. A value of unity for

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Table 3. Relatives Electronic Energies (ΔE) at Different Levels of Theory for Some Stationary Points of the (2 + 3) Cycloaddition Pathway

	MP2		MP4(SDTQ)		CCSD(T)		B3LYP	
molecule	1[a]	2[a]	1	2	1	2	1	2
TS1/2	−0.6	1.7	2.9	6.3	5.2	8.6[b]	6.9	10.4
2	−37.6	−32.4	−33.5	−28.0	−37.7	−32.2[b]	−33.3	−27.6
3	−19.2	−14.8	−19.5	−13.6	−22.2	−16.3[b]	−23.5	−15.5
TS3/2	−14.1	−10.7	−14.6	−8.3	−16.7	−10.4[b]	−17.9	−8.2

[a] Basis set 1: 6-31G+(d,p); basis set 2: 6-31+G(d,p),S(3df). [b] Calculated using the additivity approximation: ΔE[CCSD(T)/6-31G+(d,p),S(3df)] ≈ ΔE[CCSD(T)/6-31G+(d,p)] + ΔE[MP4/6-31G+(d,p),S(3df)] − ΔE[MP4/6-31G+(d,p)].

$\langle S^2\rangle$ indicates a pure diradicaloid state, consisting of an equal mixture of singlet and triplet states. The spin-correction procedure proposed by Yamaguchi and coworkers[22] has been used to obtain spin-projected energies, although the use of this technique is still a mater of debate.[23] Spin-projected corrections cannot induce larges changes in the energetic profile of the various pathways (vide infra)

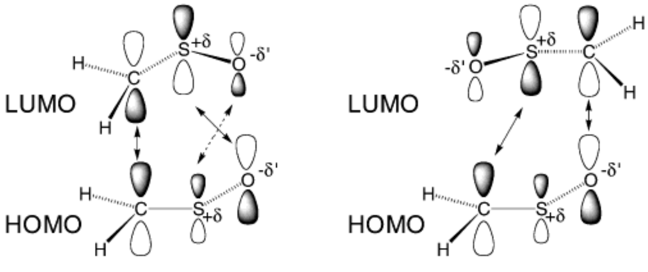
$$ {}^1E_{\mathrm{SP}} = {}^1E_{\mathrm{UB}} + f_{\mathrm{SC}}[{}^1E_{\mathrm{UB}} - {}^3E_{\mathrm{UB}}] \quad \text{with} \quad f_{\mathrm{SC}} \cong \frac{{}^1\langle S^2\rangle}{{}^3\langle S^2\rangle - {}^1\langle S^2\rangle} \quad (1) $$

The spin-correction results in a reduction in energy of 0.2 kcal/mol for **3** and 2.0 kcal/mol for **TS3/2**. These values are upper limits, according to Houk and coworkers, who point out, in their DFT study of the mechanism of the [4 + 2] cycloaddition reaction of butadiene and ethylene,[13b] that diradical energies likely take place between the corrected ${}^1E_{\mathrm{SP}}$ and the uncorrected ${}^1E_{\mathrm{UB}}$ values. Since we find that the two pathways involve passage via the same transition state, reaction dynamics calculations would be necessary to compute the partitoning between these pathways; such calculations are outside the scope of this work.

To assess the reliability of B3LYP calculations for these sulfur-containing species, some possessing a biradical character, we have performed post-HF calculations up to the CCSD(T) level for representative systems. Results are summarized in Table 3; for the purpose of comparison, B3LYP results are also added in Table 3.

When the 6-31G(d,p) basis set is used, one can notice, for the step connecting the reactants to **TS1/2(3)**, that the energy barrier is very sensitive to the level of theory: at the MP2 level, a negative barrier is found; the higher CCSD(T) level predicts a barrier equal to 5.2 kcal/mol. The relative energies of the diradical systems (**3** and **TS3/2**) are less dependent on the level of theory. A pleasant result is that B3LYP and CCSD(T) calculations provide similar pictures of this part of the potential energy surface. The inclusion of a 3df set of polarization functions on S atoms has a noticeable effect on the calculated relative energies. Increasing the basis size lowers the energy difference among **2**, **3**, **TS2/3**, and the reactants and raises the energy difference between **TS1/2** and the reactants. This effect is more pronounced for B3LYP than forMP2 and MP4 calculations. Taking CCSD(T)/6-31+G(d,p),S(3df) results as a reference, B3LYP calculations underestimate the relative stability of intermediate **3** and adduct **2** by 0.8 and 4.6 kcal/mol, respectively, and overestimate by ≈2 kcal/mol the relative energy of the transition states. However, the overall profile of the two pathways is correctly reproduced at the B3LYP level. This comparison allows us to think that a fairly accurate description of the dimerization of the sulfine is obtained at the B3LYP/6-31+G(d,p),S(3df) level.

Scheme 3



head-to-head approach (TS1/2(3)) head-to-tail approach (TS1/4)

Finally, we discuss briefly the structures in terms of NLMO/NPA bond orders, which may give further insight than the one arising from geometrical data. If bond lengths and bond orders are in accordance to attribute a very asynchrone character to **TS1/2(3)**, bond order analysis indicates for **2**, on the contrary of bond distances (see Figure 1), that the strengths of S_2-O_6 ($n_{SO} = 0.556$) and S_5-O_6 ($n_{SO} = 0.555$) bonds are nearly the same. In the same way, bond orders are more suitable than bond lengths to predict bond making in **TS3/2**: $d_{SO} = 3.121$ Å, $d_{SO} = 3.239$ Å; $n_{SO} = 0.034$, $n_{SS} = -0.005$.

Regiochemistry of the (2 + 3) Cycloaddition Reaction: Head-to-Tail Cycloaddition. Calculations predict for this approach a concerted reaction: the transition structure **TS1/4** has been located which leads to the cycloadduct **4**. At the sight of forming bond lengths (d_{CS} = 2.527 Å, d_{CO} = 1.964 Å; see Figure 1) and especially NLMO/NPA bond orders ($n_{CS} = 0.191$, $n_{CO} = 0.266$), it appears that **TS1/4** is much less asynchronous than **TS1/2**. The corresponding energy barrier $\Delta E^{\ddagger}$ is equal to 16.1 kcal/mol (17.3 with the larger basis set) and it is 5.7 kcal/mol higher than the one calculated for the head to head approach. This process is predicted to be less exothermic than the former one by 12.4 (13.2) kcal/mol; inclusion of ZPE and thermal corrections, as well as entropy terms (Table 2), only slightly modifies these differences. Thus, the pathway toward **2** is favored over the one toward **4** via **TS1/4**.

As depicted in Scheme 3, the preference for a head-to-tail transition structure cannot be understood from simple FMO arguments insofar as, in the LUMO of H_2CSO, the p_π components on carbon and sulfur atoms are almost the same. Irrespective of the fact that product **2** is more stable than **4**, secondary orbital interaction (dashed arrow <- - - -> in Scheme 3) probably favors **TS1/2(3)**; in addition, Coulombic interactions are expected to be more stabilizing in **TS1/2(3)** than in **TS1/4** (see Scheme 3; natural population analysis indicates that δ and δ' are of the order of unity).

(2 + 2) Cycloaddition Head-to-Head Approach. Inspection of the reactant MOs suggests that a concerted $[2_s + 2_s]$ process involving C−C bond formation (see Scheme 3) should be thermally forbidden. The HOMO and LUMO of sulfine have a large p_π orbital component on carbon atom, and one expects rather a stepwise

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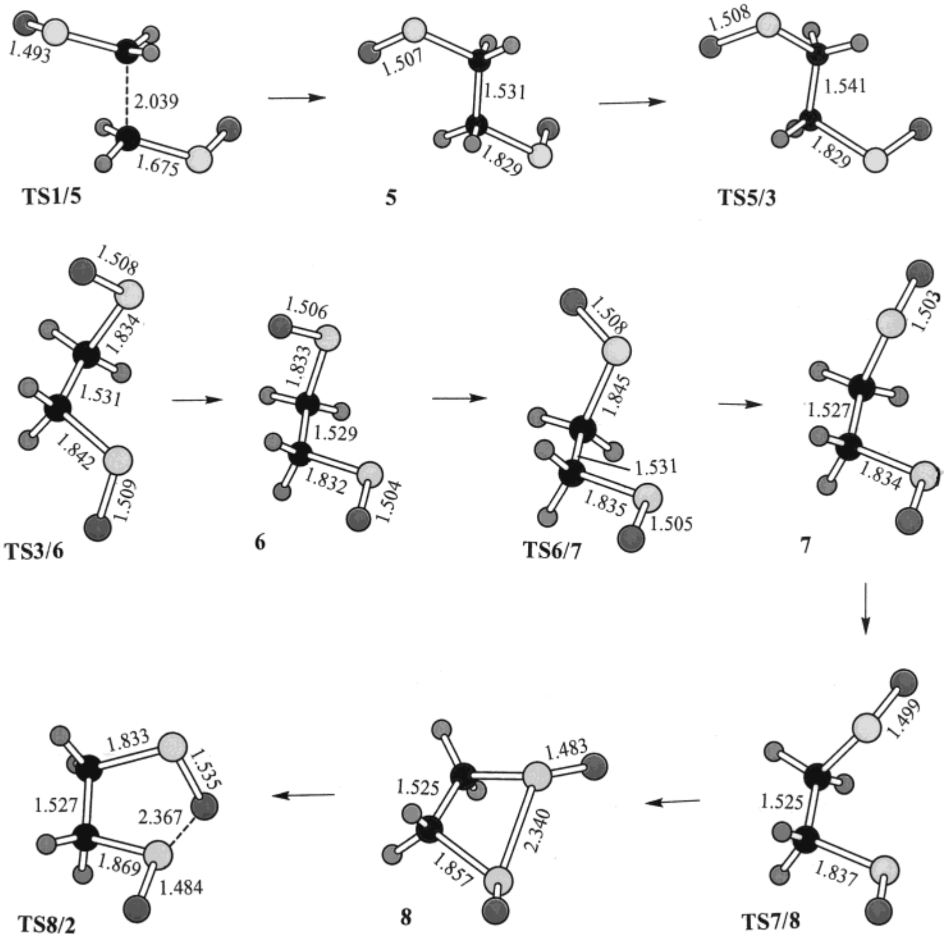

Figure 2. Summary of the reaction pathways via the anti-diradical transition state **TS1/5** and selected geometric parameters for relevant species optimized at the B3LYP:6-31+G(d,p),S(3df) level.

pathway involving first C−C bond formation. Effectively, any attemps to locate a transition state leading in one step to a four-membered ring product failed.

Table 4. Relative Electronic Energies (ΔE), Zero Point Energy Correction [Δ(ZPE)], Enthalpies (ΔH) (298.15 K), and Entropies (ΔS) (298.15 K) for the (2 + 2) Cycloaddition Reaction

molecule	$\Delta E^{a,c}$	Δ(ZPE)^a	$\Delta H^{a,c}$	ΔS^b
TS1/5	13.1 (12.5)	1.6	14.3 (13.7)	−35.6
5	−15.7 (−13.6)	3.1	−12.8 (−10.7)	−36.2
TS5/3	−13.3 (−10.7)	2.9	−11.1 (−8.5)	−39.2
TS3/6	−13.3 (−10.7)	2.9	−11.2 (−8.6)	−39.9
6	−14.4 (−12.2)	3.0	−11.6 (−9.4)	−37.2
TS6/7	−12.2 (−9.9)	2.8	−10.1 (−7.8)	−39.2
7	−14.0 (−11.9)	2.8	−11.3 (−9.2)	−39.2
TS7/8	−13.9 (−11.85)	3.1	−11.7 (−9.6)	−42.4
8	−19.6 (−17.9)	4.0	−16.4 (−14.7)	−43.4
TS8/2	−6.2 (−4.3)	3.8	−3.6 (−1.7)	−46.5
9	−7.1 (−4.9)	3.3	−4.7 (−2.5)	−45.8
TS1/9	32.7 (33.7)	5.6	33.4 (34.4)	−41.7

[a] In kcal/mol. [b] In cal/mol/K. [c] Values in parentheses correspond to single point 6-311+G(3df,2p)//6-31+G(d,p),S(3df) calculations.

Starting from a [$2_s + 2_s$] or [$2_s + 2_a$] arrangement of the two sulfine molecules, the anti transition state **TS1/5** corresponding to the formation of the C−C bond has been located and leads to the biradical intermediate **5** (see Figure 2), characterized by a SCCS dihedral angle equal to 176.1°. By rotation around the single C−C bond, the biradical intermeditate **3** mentioned above (SCCS = 289.0°) has been reached via the transition state **TS5/3** (SCCS = 234.0°). The corresponding energies are presented in Table 4. The first transition state **TS1/5** lies 13.1 kcal/mol above the reactants and the reaction energy for the **1** → **5** step is equal to −17.7 kcal/mol. For the ethylene dimerization, these values become 40.3 and 39.0 kcal/mol, respectively.[13h] One can notice that the anti-biradical TS, corresponding to the ethylene dimerization is reached for a C−C distance equal to 1.796 Å, a value which is 0.243 Å shorter than the one calculated for **TS1/5**. The early TS corresponds to the more exothermic process, in accordance with the Hammond postulate.[24] The energy difference between **TS1/5** and **TS1/2(3)** is equal to 2.7 kcal/mol. This energy difference is reduced to 1.1 kcal/mol by the use of a larger basis set. The inclusion of entropy corrections favors slightly **TS1/5**, but **TS1/2(3)** remains lower in terms of Gibbs energy by 2.8 (1.3)/kcal mol. **TS1/5** does not present any diradical character and the spin correction (eq 1) lowers the energies of **5** and **TS5/3** by 0.4 and 0.1 kcal/mol, respectively. Thus, it seems that the mechanism involving **TS1/5** becomes less favorable.

The weak energy barrier (≅2.5 kcal/mol) calculated for the **5** → **3** step suggests an easy rotation around the C−C bond of **5**. In fact, numerous rotamers of **3** with similar stability can be located on the potential energy surface, the rotation around the C−S bond being also an easy motion. An alternative **3** → **2** pathway is also given in Figure 2: a rotation around one of the C−S bond leads to the intermediate **6** via **TS3/6** (dihedral angle CCSO:

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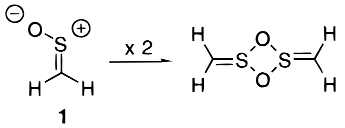
(24) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Scheme 4



318.0°(**3**), 230.5°(**TS3/6**), and 173.6°(**6**)). Similarly, the intermediate **7** is obtained by rotation around the second C−S bond. Examination of Table 4 shows that these rotations correspond to a very flat portion on the potential energy surface: the first rotation barrier (**TS3/6**) is equal to 2.2(2.6) kcal/mol and to 2.4 (2.8) kcal/mol when spin corrections are taken into account. Nonpotential energy terms lower the barrier by about 1 kcal/mol. Similar values are obtained for the second rotation barrier (**TS6/7**). At the 6-31+G(d,p)S(3df) level a very weak barrier (0.1 kcal/mol) is found for the **7** → **8** step, which implies a rotation around the C−C bond. Inclusion of spin correction lowers the energies of **7** and **TS7/8** by 0.1 and 2.3 kcal/mol, respectively. Thus, the barrier disappears at this level of calculation, and the use of the larger basis set emphasizes this tendancy. Consequently, the existence of **7** and **TS7/8** as stationary points on the potential energy surface is questionable.

Starting from a dihedral SCCS angle equal to 290.4°(**6**), intermediate **8** is reached for a SCCS value of 30.8° and for a distance between the two sulfur atoms equal to 2.340 Å; the corresponding bond order is equal to 0.780. It is worth noting that **8** is the expected product resulting from a hypothetical $[2_s + 2_s]$ head-to-head concerted cycloaddition. **8** is more stable than **6** by 5.2 (5.7) kcal/mol; this difference is reduced by inclusion of nonpotential energy correction and entropy. Finally, **8** may be converted to **2** via **TS8/2**, which is reached by an "asymmetric conrotatory" process (rotation around one of the C−S bond being more effective than the other). The barrier height for this step is calculated to be 13.4 (13.6) kcal/mol, and it is lowered by 0.6 kcal/mol when ZPE and thermal corrections are added. However, **TS8/2** is 17.9 (15.4) kcal/mol more stable than **TS1/5**, and this pathway is a viable alternative to the "direct" one.

Head-to-Tail (2 + 2) Concerted Approach. Two possibilities can be considered: simultaneous formation of O−S or C−S bonds. In the former case (Scheme 4), the expected C_{2v} four-membered ring is not a stable structure. It lies 113.6 kcal/mol above the reactants and corresponds to a second-order TS (two imaginary frequencies, 1993.7i and 811.6i cm^{-1}).

On the other hand, the C_{2v} four-membered ring **9** (see Figure 3) corresponds to a minimun on the potential surface and lies 7.1 (4.9) kcal/mol below the reactants (Table 3). The **1** → **9** step involves the **TS1/9**, which is reached for a "pseudo-$[2_s + 2_a]$" approach of the two sulfine molecules (see Figure 3). This result is in accordance with simple FMO arguments which state that a $[2_s + 2_s]$ approach is symmetry-forbidden. The large activation energy calculated for this step (33.4 (34.4) kcal/mol) indicates that **9** is a minor product for a kinetic reason. This result is in accordance with the proposals of Block and co-workers.[3,5]

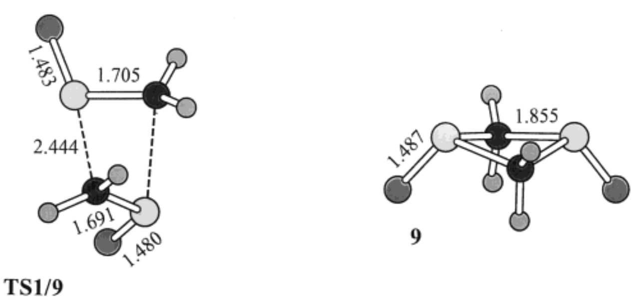


Figure 3. Some selected distances of the transition structure and the cycloadduct of the concerted $[2_s + 2_a]$ reaction, calculated at the B3LYP:6-31+G(d,p),S(3df) level.

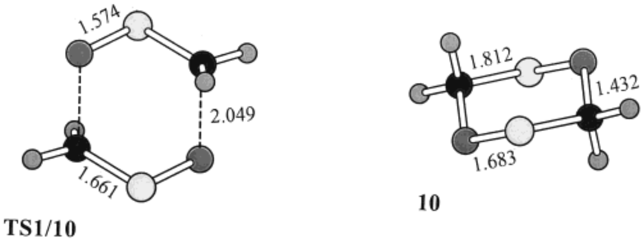


Figure 4. Some selected distances of the transition structure and the cycloadduct of the concerted (3 + 3) reaction, calculated at the B3LYP:6-31+G(d,p),S(3df) level.

Table 5. Relative Electronic Energies (ΔE), Zero Point Energy Correction [Δ(ZPE)], Enthalpies (ΔH) (298.15 K), and Entropies (ΔS) (298.15 K) for the (3 + 3) Cycloaddition Reaction

molecule	$\Delta E^{a,c}$	Δ(ZPE)^a	$\Delta H^{a,c}$	ΔS^b
TS1/10	31.4 (32.7)	1.7	32.3 (33.6)	−43.5
10	−15.3 (−14.1)	5.1	−11.5 (−10.3)	−47.7

[a] In kcal/mol. [b] In cal/mol/K. [c] Values in parentheses correspond to single point 6-311+G(3df,2p)//6-31+G(d,p),S(3df) calculations.

(3 + 3) Cycloaddition. FMO analysis suggests that a concerted (3 + 3) approach of the two sulfine molecules to lead to a six-membered transition structure will be a difficult process (see the phasing of the frontier orbitals in Scheme 3). Such a pathway (C_2 symmetry constraint) leads to a chair-conformed six-membered ring in which C−C and O−O bond lengths are respectively equal to 1.515 and 2.164 Å; this cycloadduct lies 14.0 kcal/mol above **1**. Efforts to locate the concerted transition structure for this (3 + 3) approach resulted in the location of a stationary point also characterized by large differences in C−C and O−O distances (1.689 and 2.827 Å, respectively). This structure is 17.7 kcal/mol higher in energy than reactants. But, harmonic frequency calculation identified this structure as a second-order saddle point (two imaginary frequencies at 138.2i and 117.6i cm^{-1}). Reoptimizing this second-order saddle point, by always keeping C2 symmetry and using a spin-unrestricted formalism, again led to a second-order saddle point which lies 14.8 kcal/mol above **1**. Thus, the cycloadduct **13** (Scheme 2) cannot be formed from **1**. On the other hand, a first-order transition state **TS1/10** corresponding to the formation of two identical C−O bonds (concerted head-to-tail approach) has been identified; this structure, as well as the one of the resulting six-membered ring adduct **10**, is represented in Figure 4; the corresponding energies are given in Table 5.

Judging by the S−O distance and n_{SO} NLMO/NPA bond order (0.175 in **TS1/10** and 0.651 in **10**), the extent of bond formation in **TS1/10** is relatively more important than the one encountered for the other transitions structures. As expected, this process requires an activation energy of 32.3(33.6) kcal/mol, 20 kcal/mol larger than the one calculated for the rate-determining step of the

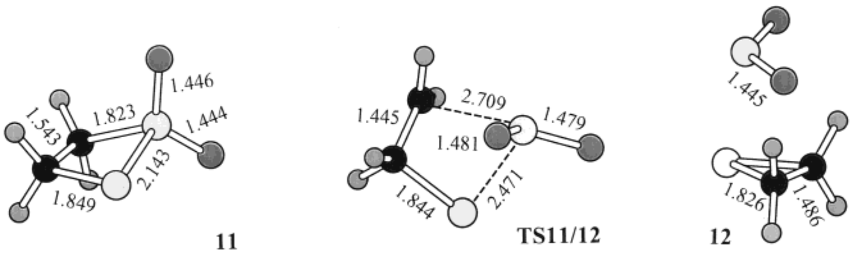


Figure 5. Summary of the decomposition reaction of **11** and selected geometric parameters for relevant species optimized at the B3LYP:6-31+G(d,p),S(3df) level.

Table 6. Relative Electronic Energies (Δ*E*), Zero Point Energy Correction [Δ(ZPE)], Enthalpies (Δ*H*) (298.15 K), and Entropies Δ*S* (298.15 K) for the Reaction Decomposition of 11

molecule	$\Delta E^{a,c}$	Δ(ZPE)^{a}	$\Delta H^{a,c}$	ΔS^{b}
11	−34.9 (−33.9)	5.5	−30.6 (−29.6)	−45.7
TS11/12	12.2 (13.3)	2.3	13.9 (15.0)	−40.4
12 [SO_2+ $S(CH_3)_2$]	−34.8 (−34.8)	2.4	−32.8 (−32.8)	−3.2

[a] In kcal/mol. [b] In cal/mol/K. [c] Values in parentheses correspond to single point 6-311+G(3df,2p)//6-31+G(d,p),S(3df) calculations.

(3+2) cycloaddition. This approach did not appear to be a viable process despite its moderate exothermicity of about 10 kcal/mol. Although **10** is expected less constraint than **2**, it is calculated 12 kcal/mol less stable.

Attempt To Obtain the Four-Membered Ring 11. As mentionned in the Introduction, the expected final term of the sulfine dimerization is the cycloadduct **11**, depicted in Figure 5.

The CCSS ring is almost planar (CCSS dihedral angle equal to 15.2°). This is the most stable of the cycloadducts described in this work (see Table 6). Particularly, **11** lies about 7 kcal/mol below **2** and then the postulated **2** → **11** step is predicted exothermic.[25] However, despite an extensive search, we were unable to find a reaction path for this rearrangement.

With regard to this situation, we have searched for possible transformations of **11** with the aim to suggest another interconversion scheme. The only reaction path located corresponds to the decomposition of **11** into SO_2 and $S(CH_2)_2$ (see Figure 5). This process occurs via **TS11/12**, which lies 12.2 (13.3) kcal/mol above the two sulfine molecules. This decomposition is predicted to be slightly exothermic by 2−3 kcal/mol and necessitates an activation barrier equal to 44.5 kcal/mol (see Table 6). Thus, our goal to find a channel connecting **2** to **11** has failed.

Conclusions

In this paper we have investigated the dimerization of the sulfine **1** using a DFT computational approach based on the B3LYP functional. On both thermodynamic and kinetic grounds, the head-to-head (2 + 3) cycloadduct **2** should be the preferred primary dimerization product. This reaction pathway is decidedly asynchronous and a stepwise mechanism involving a biradical intermediate appears reasonable also. Another less favorable multistep channel occurs via an anti transition state, which leads also to **2** as the final term. In line with the proposal of Block and co-workers, our results indicate that the four-membered ring **9** cannot be considered as the main product of the sulfine dimerization. However, we were unable to corroborate by calculations the other proposal of the Block group, i.e., interconversion of **2** into the more stable four-membered ring **11**. Further researchs, including solvent effects, will be necessary to elucidate this point. It is noteworthy that the main results of this work can be readily explained in terms of frontier molecular orbital theory.

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[25] At this point, one emphasizes the influence of the basis set on the relative energies of the various isomers: at the B3LYP/6-31+G(d, p)//B3LYP/6-31+G(d, p) level, **11** is predicted to be 1.7 kcal/mol more stable than **2**.