

An ab Initio and Density Functional Theory Study of the Structure and Bonding of Sulfur Ylides

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Sulfur ylides are useful synthetic intermediates that are formed from the interaction between singlet carbenes and sulfur-containing molecules. Partial double-bond character frequently has been proposed as a key contributor to the stability of sulfur ylides. Calculations at the B3LYP, MP2, and CCSD(T) levels of theory employing various basis sets have been performed on the sulfur ylides $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ in order to investigate the structure and bonding of these systems. The following general properties of sulfur ylides were observed from the computational studies: C–S bond distances that are close in length to that of a typical C–S double bond, high charge transfer from the sulfide to the carbene, and large torsional rotation barriers. Analysis of the sulfur ylide charge distribution indicates that the unusually short C–S bond distance can be attributed in part to the electrostatic attraction between highly oppositely charged carbon and sulfur atoms. Furthermore, $n \rightarrow \sigma^*$ stabilization arising from donation of electron density from the carbon lone pair orbital into S–H or S–C antibonding orbitals leads to larger than expected torsional barriers. Finally, natural resonance theory analysis indicates that the bond order of the sulfur ylides $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ is 1.4–1.5, intermediate between a single and double bond.

1. Introduction

Sulfur ylides are important intermediates in chemical reactions that are formed from the interaction between a molecule that contains a sulfur atom and a singlet carbene.¹ It is generally postulated that a sulfur ylide forms when electron density from a lone pair orbital on the sulfur atom is donated into the empty p_z -type orbital on the carbon atom of the carbene. Because of their generally high reactivities and relatively short lifetimes, ylides are prime candidates for investigation by computational methods.

The simplest ylides are relatively small in size, and therefore high-level molecular orbital calculations are feasible. Early correlated ab initio calculations of sulfur ylides probed their structure, bonding, and energetics.^{2–4} For example, in work by Yates et al.,⁴ the optimized geometry of the ylide formed between H_2S and CH_2 was obtained at the MP2/6-31G(d) level of theory, and improved relative energies were determined at the MP4/6-311G(df,p)//MP2/6-31G* level. These authors found that the C–S and C–P bonds of sulfur and phosphorus ylides, respectively, were significantly shorter than typical single bonds of the same type.

In addition to the early computational work on sulfur ylides, some studies of specific sulfur ylides also have recently appeared in the literature.^{5–10} Jursic has studied the sigmatropic rearrangement of allylic sulfur ylides using ab initio methods.⁵ Shimizu et al. have investigated pyramidal inversion of sulfur, selenium, and tellurium ylides at the MP2/DZP level of theory.⁶ Platz and co-workers have studied the sulfur ylide formed from ethylene sulfide and methylene at the HF, MP2, B3LYP, and CASSCF(4,4) levels of theory;⁷ the rearrangement of the ylide

via various pathways was explored and compared to experiment. Density functional theory (DFT) methods have been employed recently to explore the mechanism for formation of epoxides from the reaction of sulfur ylides with aldehydes.^{8,9} Finally, another recent DFT study probed the mechanism of formation of aziridine in solution from the reaction of a sulfur ylide with an imine.¹⁰

Partial double-bond character in sulfur and phosphorus ylides frequently has been proposed as a contributor to their enhanced stabilities relative to other ylides such as their oxygen and nitrogen analogues.^{1,11,12} Two main resonance structures, shown in Figure 1, are thought to play a role in sulfur ylide stabilization. Early investigators proposed that the partial double-bond character of sulfur and phosphorus ylides arose from overlap of d-type orbitals on sulfur with a p-type orbital on the carbene carbon, resulting in $p_\pi-d_\pi$ type back-bonding.^{1,4} Other workers have suggested that the bonding in sulfur and phosphorus ylides could be represented in terms of two distinct banana bonds.² More recent analysis of the bonding in phosphorus ylides suggests that negative hyperconjugation, involving transfer of electron density from a filled orbital on the carbene carbon to an antibonding orbital on the heteroatom-containing species, may give rise to the partial double character.^{11,12}

A recent computational study probed the character of the bonding in a series of N-, P-, As-, O-, S-, and Se-containing ylides.¹³ Some conflicting results were obtained with respect to the double bond character of the S–C bond in $\text{H}_2\text{S}-\text{CH}_2$. The atoms in molecules (AIM) analysis found evidence of multiple bond character for the sulfur ylide bond; however, the computed NMR chemical shifts were very similar to those of single-bonded systems. Other recent studies by Mitrasinovic investigated the bonding in sulfur and phosphorus ylides based on a sharing analysis of the electron density.^{14–16} For sulfur ylides, the sharing indices suggested a C–S bond strength

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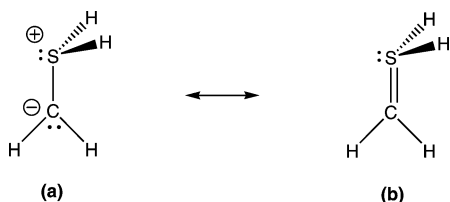


Figure 1. (a) Single- and (b) double-bonded resonance structures of the $\text{H}_2\text{S}-\text{CH}_2$ sulfur ylide.

intermediate between a single and double bond. In addition, group basin charges and intergroup sharing indices indicated a highly polar double bond between the carbon and sulfur.

One of the other interesting properties of sulfur ylides is related to the torsional barrier for rotation about the C–S ylide bond. Early computational work at the Hartree–Fock level with a DZP basis set compared the rotation barriers of ylides formed between methylene and compounds containing first- and second-row heteroatoms (N, O, P, and S).¹⁷ The rotation barriers of the first-row ylides $\text{H}_2\text{O}-\text{CH}_2$ and $\text{H}_3\text{N}-\text{CH}_2$ were determined to be similar and relatively small, 2.3 and 5.6 kcal/mol, respectively. In contrast, the rotation barrier of the phosphorus ylide $\text{H}_3\text{P}-\text{CH}_2$ was calculated to be 0.2 kcal/mol, while that of the sulfur ylide $\text{H}_2\text{S}-\text{CH}_2$ was determined to be 21.2 kcal/mol, quite high compared to the other ylides.

Because of the synthetic utility of sulfur ylides, a clearer understanding of the structure and properties of these compounds from computational investigations should provide the opportunity for additional insight into their behavior. In this paper, *ab initio* and density functional theory calculations to determine the geometries, energetics, and bonding of sulfur ylides are reported. The sulfur ylides studied are those formed from interaction of singlet methylene with either hydrogen sulfide or dimethylsulfide in order to provide comparisons with previous work. In particular, the focus is on understanding the origins of the shortened C–S bond in sulfur ylides along with the relatively high torsional barrier for rotation about the C–S bond. To better understand the details of the bonding of sulfur ylides, natural population,¹⁸ natural bond orbital,¹⁹ and natural resonance theory^{20,21} analyses have been performed on each of the ylides.

2. Methods

Full geometry optimizations were carried out at the MP2 and B3LYP levels of theory for the monomers CH_2 , H_2S , and $(\text{CH}_3)_2\text{S}$ as well as for the ylides $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ using correlation-consistent basis sets, referred to as aug-cc-pVXZ (X = D, T, and Q), for basis sets of split-valence double- ζ to quadruple- ζ quality augmented with diffuse and polarization functions. For comparison with molecules containing typical single and double C–S bonds, geometry optimiza-

tions also were performed on the molecules CH_3SH and H_2CS . It has been shown that the use of “tight” d-type polarization functions on sulfur is helpful in improving the description of the structure and the energetics of some sulfur-containing compounds.^{22–25} Therefore, the basis sets for sulfur included additional tight d-type polarization functions as described by Dunning and co-workers²⁶ and are referred to as aug-cc-pV-(X+d)Z (X = D, T, and Q). Geometry optimizations were carried out using tight convergence criteria, and stationary points were verified by calculation of harmonic vibrational frequencies. For the $\text{H}_2\text{S}-\text{CH}_2$ ylide, additional geometry optimizations were performed using the CCSD(T) method with the same correlation-consistent basis sets.

Binding energies of the ylides were calculated relative to the separated monomers and were corrected to account for vibrational zero-point energies. The torsional barriers for rotation about the C–S bond in the ylides were determined by locating transition states, which were verified by the presence of a single imaginary frequency. The torsional barrier for rotation about the C–S single bond in $(\text{CH}_3)_2\text{S}$ also was determined for comparison with the ylide barriers.

Natural population, natural bond orbital, and natural resonance theory analyses were performed using the NBO 5.0 software package.²⁷ These calculations were utilized to obtain information about the charge transfer from the sulfide to the carbene in the ylides as well as to provide insight into the character of the bonding of the ylides.

All the B3LYP and MP2 calculations were performed using the Gaussian03 software package.²⁸ The CCSD(T) calculations were carried out using the Molpro software package.²⁹ Linux workstations at Illinois State University were employed for most of the calculations, though some of the larger calculations were carried out on the IBM p690 computer at the National Center for Supercomputing Applications.

3. Results and Discussion

A. Structure and Energetics. Table 1 presents the C–S ylide bond lengths computed for the $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ ylides at the B3LYP and MP2 levels of theory and in addition for $\text{H}_2\text{S}-\text{CH}_2$ at the CCSD(T) level. Also listed in the table for comparison are C–S bond lengths of compounds with known single and double bonds, CH_3SH and H_2CS . The atom-numbering scheme of the ylides is illustrated in Figure 2. Cartesian coordinates, electronic energies, and vibrational zero-point energies of the optimized ylides are included in the Supporting Information.

The calculated C–S ylide bond distances of $\text{H}_2\text{S}-\text{CH}_2$ are in accord with previous computational results, which fall in the range of 1.64–1.70 Å from calculations employing various levels of theory and basis set choices.^{2,4,6,13,17} The current results

TABLE 1: C–S Bond Length Comparisons between Sulfur Ylides and Compounds Containing C–S Single and Double Bonds

level of theory/basis set	C1–S4 distance (Å) ^a			
	$\text{H}_2\text{S}-\text{CH}_2$	$(\text{CH}_3)_2\text{S}-\text{CH}_2$	CH_3SH	H_2CS
B3LYP/aug-cc-pV(D+d)Z	1.664	1.651	1.829	1.615
B3LYP/aug-cc-pV(T+d)Z	1.646	1.641	1.824	1.607
B3LYP/aug-cc-pV(Q+d)Z	1.644	1.639	1.823	1.606
MP2/aug-cc-pV(D+d)Z	1.669	1.660	1.820	1.621
MP2/aug-cc-pV(T+d)Z	1.639	1.633	1.804	1.605
MP2/aug-cc-pV(Q+d)Z	1.634	1.629	1.803	1.603
CCSD(T)/aug-cc-pV(D+d)Z	1.693			
CCSD(T)/aug-cc-pV(T+d)Z	1.664			
CCSD(T)/aug-cc-pV(Q+d)Z	1.655			

^a The atom-numbering scheme for the ylides is shown in Figure 2.

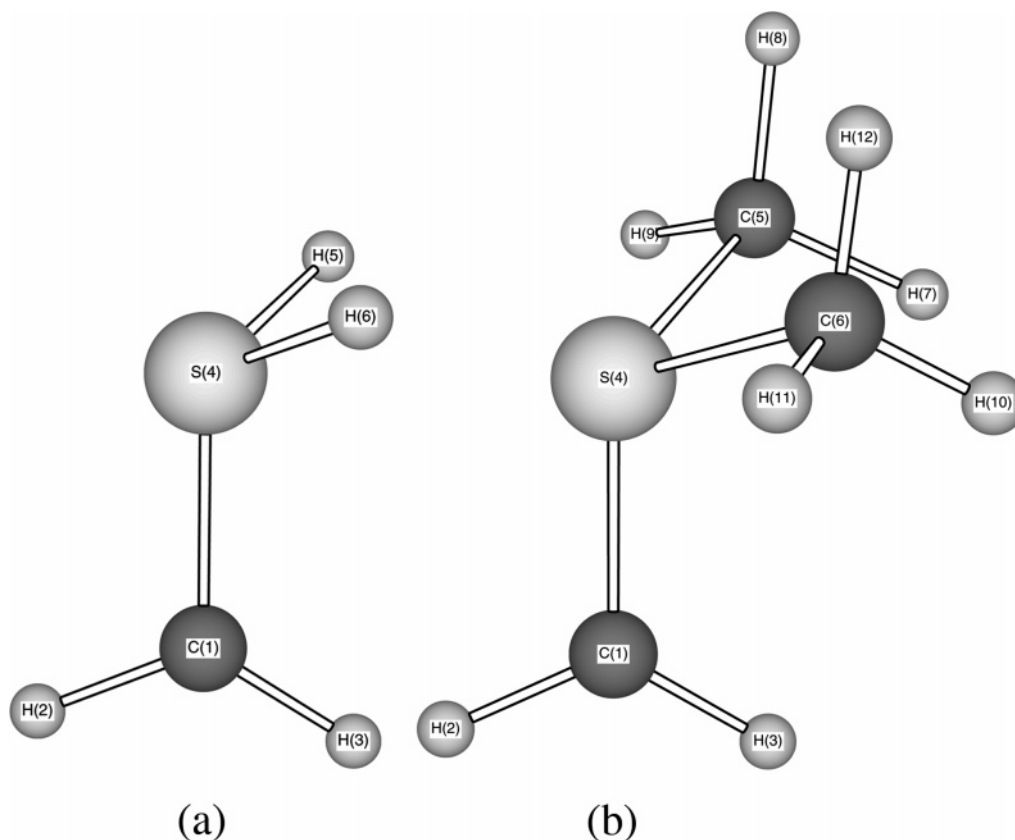


Figure 2. Optimized geometries of (a) $\text{H}_2\text{S}-\text{CH}_2$ and (b) $(\text{CH}_3)_2\text{S}-\text{CH}_2$ obtained at the MP2/aug-cc-pV(T+d)Z level of theory.

predict the C–S ylide bond distance of $\text{H}_2\text{S}-\text{CH}_2$ to be in the range 1.64–1.66 Å using the B3LYP method and 1.63–1.67 Å using the MP2 method. The C–S ylide bond distance of $(\text{CH}_3)_2\text{S}-\text{CH}_2$ is only slightly shorter than that of $\text{H}_2\text{S}-\text{CH}_2$, differing by only 0.005 Å for calculations using the aug-cc-pV(Q+d)Z basis set. It also should be noted that ylide bond lengths computed at the CCSD(T) level of theory are somewhat longer than those determined using either the B3LYP or MP2 methods. For the $\text{H}_2\text{S}-\text{CH}_2$ ylide, the C–S bond distance computed using the CCSD(T)/aug-cc-pV(Q+d)Z method is 0.01 Å longer than that obtained using the B3LYP method and 0.02 Å longer than that obtained using the MP2 method and the same basis set.

The C–S ylide bond distance of an ylide similar to those studied in this work, $(\text{CH}_3)_2\text{S}-\text{C}(\text{CN})_2$, has been determined experimentally to be 1.73 Å in the crystal,³⁰ slightly longer than the bond lengths for the sulfur ylides studied in this work. We have carried out gas-phase geometry optimizations of $(\text{CH}_3)_2\text{S}-\text{C}(\text{CN})_2$ at the B3LYP and MP2 levels of theory using the aug-cc-pV(T+d)Z basis set and have obtained C–S bond lengths of 1.71 and 1.68 Å, respectively, in reasonable agreement with the reported crystal structure results. Some of the difference between the computed and crystal results for $(\text{CH}_3)_2\text{S}-\text{C}(\text{CN})_2$ also may be attributed to crystal-packing effects.

When comparing the C–S ylide bond distances to typical single and double bonds, the results clearly suggest that the ylide bond distance is more similar to a double bond than to a single-bond distance. For example, at the MP2/aug-cc-pV(Q+d)Z level of theory, the C–S single bond distance of CH_3SH is 1.80 Å, and the C–S double bond distance of H_2CS is 1.60 Å. In comparison, the C–S bond distances in the two ylides are both 1.63 Å, only slightly longer than the double bond distance.

To examine the origins of the relatively short C–S bond found in the ylides, natural population analysis was carried out.

TABLE 2: Charge Transfer of Sulfur Ylides

level of theory/basis set	charge transfer ^a	
	$\text{H}_2\text{S}-\text{CH}_2$	$(\text{CH}_3)_2\text{S}-\text{CH}_2$
B3LYP/aug-cc-pV(D+d)Z	0.563	0.595
B3LYP/aug-cc-pV(T+d)Z	0.558	0.605
B3LYP/aug-cc-pV(Q+d)Z	0.554	0.605
MP2/aug-cc-pV(D+d)Z	0.590	0.615
MP2/aug-cc-pV(T+d)Z	0.586	0.627
MP2/aug-cc-pV(Q+d)Z	0.584	0.620

^a The charge transfer is defined as the amount of charge transferred from the sulfide to methylene. The atomic charges were computed using natural population analysis.

TABLE 3: Selected Natural Atomic Charges of Sulfur Ylides and Other Sulfur-Containing Compounds

molecule	B3LYP/aug-cc-pV(T+d)Z		MP2/aug-cc-pV(T+d)Z	
	S	C	S	C
$\text{H}_2\text{S}-\text{CH}_2$	0.48	−0.98	0.52	−1.00
$(\text{CH}_3)_2\text{S}-\text{CH}_2$	0.84	−1.02	0.88	−1.04
CH_3SH	−0.04	−0.69	−0.03	−0.70
H_2CS	0.09	−0.44	0.12	−0.46

The charge transfer from the sulfide to methylene is reported in Table 2. For the ylides, a significant amount of charge transfer occurs from the sulfide to singlet methylene, ranging from 0.55 to 0.63. In comparison, the charge transfer observed for the sulfur ylides is significantly higher than that found in previous work for the analogous oxonium ylides, in which charge transfer was determined to fall in the range 0.29–0.35 at the MP2 level of theory.^{31,32}

To further explore the origins of the short C–S ylide bonds, selected natural atomic charges are presented in Table 3 for the $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ ylides and also for the compounds CH_3SH and H_2CS . In the ylides, the sulfur atom has a significant positive charge of 0.5 in $\text{H}_2\text{S}-\text{CH}_2$ and 0.8–0.9 in $(\text{CH}_3)_2\text{S}-$

TABLE 4: Binding Energy of Sulfur Ylides

level of theory/basis set	binding energy (kcal/mol) ^a	
	H ₂ S—CH ₂	(CH ₃) ₂ S—CH ₂
B3LYP/aug-cc-pV(D+d)Z	37.8	52.3
B3LYP/aug-cc-pV(T+d)Z	39.8	53.9
B3LYP/aug-cc-pV(Q+d)Z	40.3	54.4
MP2/aug-cc-pV(D+d)Z	39.9	58.6
MP2/aug-cc-pV(T+d)Z	47.4	65.6
MP2/aug-cc-pV(Q+d)Z	47.5	65.6

^a The binding energies are corrected for vibrational zero-point energies and are measured relative to the separated molecules.

CH₂, while the carbon atom possesses a substantial negative charge of about -1.0 in both ylides. On the other hand, the charge distributions of the compounds that possess typical C—S single and double bonds, CH₃SH and H₂CS, exhibit no such large charge separation. For the singly bonded compound, the charge of the sulfur atom of CH₃SH is close to zero, while the carbon possesses a negative charge of -0.7 . In the doubly bonded compound, the charge of the sulfur atom of H₂CS is positive but close to zero (~ 0.1), and the charge of carbon is negative (around -0.4). The large charge separation observed in the C—S ylide bond thus likely plays a role in the shortened C—S bond due to the attraction between the highly oppositely charged carbon and sulfur atoms. In the sharing analysis study of sulfur ylides by Mitrasinovic, the calculated group basin charges also reflected the highly polar nature of the C—S bond.¹⁴ In that work, the carbon group basin charge was calculated to be -0.4 , and the sulfur group basin charge was 0.5 .

Because the carbon and sulfur atoms that participate in the ylide bond are oppositely charged, it is expected that carbenes with electron-withdrawing substituents will exhibit longer C—S bonds due to the withdrawal of negative charge from the carbene carbon. Comparison of the bond lengths of (CH₃)₂S—CH₂ and (CH₃)₂S—C(CN)₂ confirm this effect: at the MP2/aug-cc-pV(T+d)Z level of theory, the C—S bond lengths are 1.633 and 1.685 Å, respectively. Kirmse also has noted a similar lengthening of C—P bonds in phosphorus ylides when electron-withdrawing groups are placed on the carbene.³³

The binding energies of the H₂S—CH₂ and (CH₃)₂S—CH₂ ylides are presented in Table 4. The binding energy is calculated relative to the separated monomers and is corrected for vibrational zero-point energies. For the calculation of the binding energy of (CH₃)₂S—CH₂ at the MP2/aug-cc-pV(Q+d)Z level of theory, the vibrational zero-point energies from the MP2/aug-cc-pV(T+d)Z level of theory were employed due to the computational expense involved in determining vibrational frequencies with the quadruple- ζ basis set. Basis-set superposition error corrections have not been included in the results. The sulfur ylide binding energies are fairly large, 48 kcal/mol for H₂S—CH₂ and 66 kcal/mol for (CH₃)₂S—CH₂ at the MP2/aug-cc-pV(Q+d)Z level of theory. In comparison, binding energies of the analogous oxonium ylides have been calculated to be only 10 kcal/mol for H₂O—CH₂ and 21 kcal/mol for (CH₃)₂O—CH₂ at the MP2/6-311++G(d,p) level of theory.^{31,32} In contrast, phosphorus ylides have been determined to have even stronger binding energies than sulfur ylides. For example, the binding energy of H₃P—CH₂ was computed to be 66 kcal/mol at the MP2/6-311++G(d,p) level, and the binding energy of (CH₃)₃P—CH₂ was found to be 88 kcal/mol at the MP2/6-31+G(d) level.³⁴ In support of these findings, recent computational studies also predict that phosphorus ylides have greater double bond character than sulfur ylides.^{14–16}

B. Torsional Rotation Barriers. Early computational work at the Hartree–Fock level on sulfur ylides provided evidence

TABLE 5: Torsional Rotation Barriers (kcal/mol) of Sulfur-Containing Compounds

level of theory/basis set	(CH ₃) ₂ S	H ₂ S—CH ₂		(CH ₃) ₂ S—CH ₂	
		TS1 ^a	TS2	TS1	TS2
B3LYP/aug-cc-pV(D+d)Z	1.70	14.67	13.34	14.99	9.56
B3LYP/aug-cc-pV(T+d)Z	1.72	15.54	14.37	15.42	10.36
B3LYP/aug-cc-pV(Q+d)Z	1.72	15.66	14.55	15.49	10.46
MP2/aug-cc-pV(D+d)Z	1.93	15.21	12.67	15.38	8.60
MP2/aug-cc-pV(T+d)Z	2.01	16.38	14.12	16.01	9.76
MP2/aug-cc-pV(Q+d)Z	2.04	16.64	14.73		

^a The transition states for rotation about the ylide bond are defined in Figure 3.

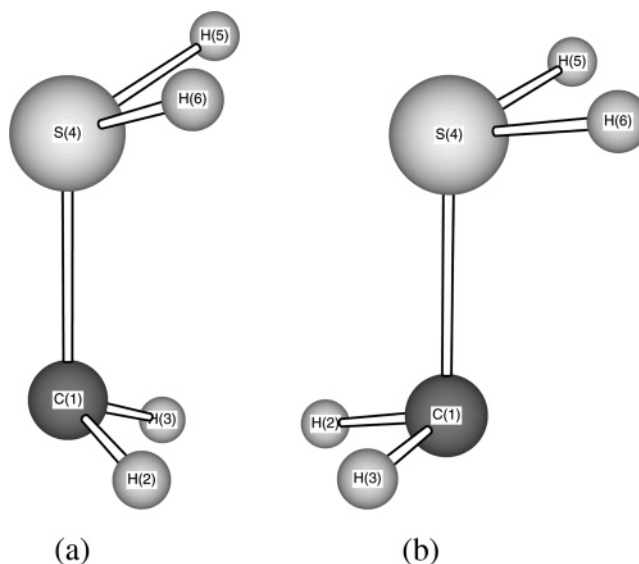


Figure 3. Transition states for rotation about the S—C bond of H₂S—CH₂ obtained at the MP2/aug-cc-pV(T+d)Z level of theory: (a) TS1; (b) TS2.

that the torsional barrier for rotation about the ylide bond was much higher for sulfur ylides than for nitrogen, oxygen, or phosphorus ylides.¹⁷ To explore torsional rotation about the C—S bond in sulfur ylides, transition states for rotation have been located and the barriers for rotation calculated, including vibrational zero-point energy corrections. Table 5 presents results obtained at the B3LYP and MP2 levels of theory for the torsional rotation barriers of the ylides H₂S—CH₂ and (CH₃)₂S—CH₂ as well as for rotation about one of the C—S bonds in the singly bonded compound (CH₃)₂S. For the (CH₃)₂S—CH₂ ylide, rotation barriers were not determined at the MP2/aug-cc-pV(Q+d)Z level due to computational expense, and for (CH₃)₂S, the vibrational frequencies obtained at the MP2/aug-cc-pV(T+d)Z level were utilized to estimate the barrier at the MP2/aug-cc-pV(Q+d)Z level. Two barriers to rotation are found for the sulfur ylides depending on the direction of rotation, labeled TS1 and TS2, as illustrated in Figure 3.

The torsional barrier for rotation about the C—S single bond in (CH₃)₂S is 1.7 kcal/mol at the B3LYP level of theory and 2.0 kcal/mol at the MP2 level of theory, determined using the aug-cc-pV(T+d)Z basis set. The sulfur ylide rotation barriers are significantly larger than those of the singly bonded compound. By use of the aug-cc-pV(T+d)Z basis set, the two barriers for rotation about the C—S bond of H₂S—CH₂ are 14.4 and 15.5 kcal/mol at the B3LYP level and 14.1 and 16.4 kcal/mol at the MP2 level. In (CH₃)₂S—CH₂, the corresponding barriers are 10.4 and 15.4 kcal/mol at the B3LYP level and 9.8 and 16.0 kcal/mol at the MP2 level.

TABLE 6: Second-Order Perturbation Theory Analysis of Interactions in Sulfur Ylides

donor–acceptor Interaction	ylide	E2 ^a (kcal/mol)	
		TS1	TS2
H ₂ S–CH ₂			
C1 lone pair → σ*(S4–H5)	23.3	7.2	3.0
C1 lone pair → σ*(S4–H6)	10.6	7.2	3.0
C1 lone pair → S4 Ryd(d)	11.2	13.0	9.9
(CH ₃) ₂ S–CH ₂			
C1 lone pair → σ*(S4–C5)	21.7	7.4	2.7
C1 lone pair → σ*(S4–C6)	12.9	7.4	2.7
C1 lone pair → S4 Ryd(d)	8.7	11.6	9.6

^a E2 is the second-order perturbation energy for the interaction between donor and acceptor orbitals calculated at the B3LYP/aug-cc-pV(T+d)Z level of theory.

To attempt to understand the origin and significance of the large torsional barrier observed for the sulfur ylides, a natural bond orbital (NBO) analysis was performed for each ylide and for the corresponding rotational transition states. The NBO analyses of the H₂S–CH₂ and (CH₃)₂S–CH₂ ylides indicate that the leading natural Lewis structure in both ylides involves a C–S single bond. The natural population of the carbon lone pair orbital ranges from 1.61 to 1.64, while none of the other orbitals in the Lewis space has an occupancy of less than 1.95. Significant non-Lewis occupancy is found in the two S–H antibonding orbitals of H₂S–CH₂ (or S–C antibonding orbitals of (CH₃)₂S–CH₂), with populations of 0.14–0.21, and in a primarily d-type Rydberg orbital on sulfur, with a population of 0.06. None of the other non-Lewis type orbitals have occupancies greater than 0.016.

In Table 6, a summary of the key findings from the NBO second-order perturbation theory analysis of the orbital interactions is presented for the equilibrium structures of H₂S–CH₂ and (CH₃)₂S–CH₂ and for the rotational transition states calculated at the B3LYP/aug-cc-pV(T+d)Z level of theory. The perturbation analysis shows that interactions between the carbon lone pair orbital and the S–H antibonding orbitals of H₂S–CH₂ or the S–C antibonding orbitals of (CH₃)₂S–CH₂ provide key stabilizing factors for the sulfur ylides. It is these $n \rightarrow \sigma^*$ stabilizing interactions that are primarily responsible for the large rotation barrier about the C–S bond. The interaction between the carbon lone pair and the S4–H5 antibonding orbital of the H₂S–CH₂ ylide is illustrated in Figure 4, generated using the NBOView software package.³⁵ The orbital shown in the lower portion of Figure 4 is the carbon lone pair orbital and in the upper portion is the S4–H5 antibonding orbital. When the ylide is rotated about the C–S bond, the overlap between the carbon lone pair orbital and the S–H antibonding orbitals drops off, destabilizing the complex and leading to a large rotation barrier.

Table 6 also indicates that there is some stabilization of the ylide due to donation of electron density from the carbon lone pair orbital into an empty d-type orbital on sulfur, though this stabilization is only about one-third that attributed to the $n \rightarrow \sigma^*$ stabilization, 11 kcal/mol compared to 34 kcal/mol for the H₂S–CH₂ ylide. This is suggestive, however, of the early discussions of the double-bond character in sulfur ylides arising from d-orbital contributions on sulfur.^{1,8,9} It is clear from the second-order perturbation analysis, though, that d-orbital participation plays only a minor role in the description of sulfur ylide bonding.

Further evidence that the $n \rightarrow \sigma^*$ interactions are primarily responsible for the large sulfur ylide torsional rotation barrier can be found from examination of the second-order perturbation analysis for the rotational transition states, also shown in Table

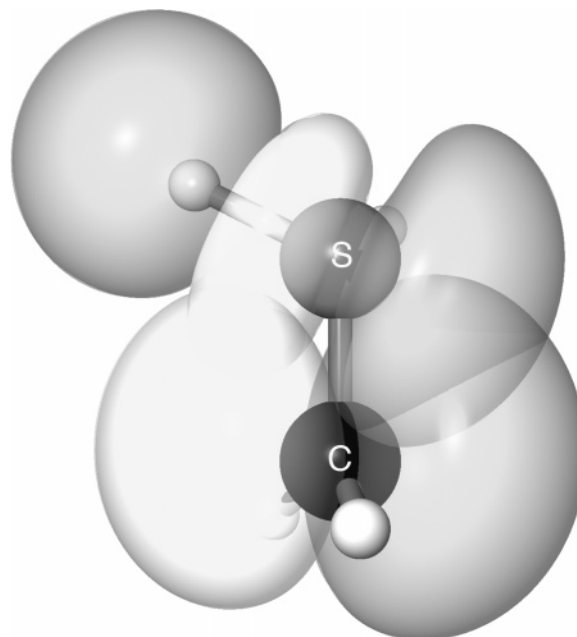


Figure 4. Overlap of the carbon lone pair (lower orbital) and S4–H5 antibonding orbital (upper orbital) of H₂S–CH₂, illustrating the key interaction responsible for the large torsional barrier for rotation about the S–C bond.

TABLE 7: NRT Bond Orders of Sulfur Ylides

level of theory/basis set	bond order	
	H ₂ S–CH ₂	(CH ₃) ₂ S–CH ₂
B3LYP/aug-cc-pV(D+d)Z	1.394	1.467
B3LYP/aug-cc-pV(T+d)Z	1.411	1.458
B3LYP/aug-cc-pV(Q+d)Z	1.427	1.457
MP2/aug-cc-pV(D+d)Z	1.378	1.382
MP2/aug-cc-pV(T+d)Z	1.409	1.394
MP2/aug-cc-pV(Q+d)Z	1.427	1.428

6. The second-order perturbation analysis of the rotational transition states shows that the $n \rightarrow \sigma^*$ stabilization energy due to interaction of the carbon lone pair orbital with the S–H antibonding orbitals of H₂S–CH₂ (or the S–C antibonds of (CH₃)₂S–CH₂) drops significantly for the transition states. For example, $n \rightarrow \sigma^*$ stabilization drops from a total of 33.9 kcal/mol for H₂S–CH₂ at its equilibrium configuration to 14.4 kcal/mol for TS1 and 6.0 kcal/mol for TS2. Furthermore, no other significant stabilizing interactions appear in the second-order perturbation analysis of the transition states, so the overall effect is lower stability.

C. Natural Resonance Theory (NRT) Analysis. To further the investigation of the single/double bond character of sulfur ylides, NRT analysis^{20,21} has been performed for each ylide. The bond orders of the C–S bonds obtained from NRT analysis are presented in Table 7 for the H₂S–CH₂ and (CH₃)₂S–CH₂ ylides. At the B3LYP and MP2 levels of theory, the NRT analysis finds a bond order of 1.38–1.43 for H₂S–CH₂ and 1.39–1.46 for (CH₃)₂S–CH₂, intermediate between a single bond and a double bond. For comparison, the NRT bond order of the C–S bond is 1.04 for CH₃SH and 2.08 for H₂CS at the B3LYP/aug-cc-pV(T+d)Z level of theory. Further examination of the NRT results suggests that the C–S bond possesses a significant ionic character. For example, for the H₂S–CH₂ ylide at the B3LYP/aug-cc-pV(T+d)Z level, the bond order of 1.41 can be decomposed into a covalent contribution of 1.03 and an ionic contribution of 0.38. For the (CH₃)₂S–CH₂ ylide at the

same level of theory, the bond order of 1.46 can be decomposed into a covalent contribution of 1.02 and an ionic contribution of 0.43.

NRT analysis also allows the bonding to be decomposed into leading resonance contributors. For example, for $\text{H}_2\text{S}-\text{CH}_2$ at the B3LYP/aug-cc-pV(T+d)Z level, the NRT analysis finds that the major resonance contributor (49%) is the singly bonded structure, as seen in Figure 1a. The doubly bonded resonance structure (Figure 1b) contributes 26%, and the remainder of the contributions come from structures with hyperconjugative interactions, with no individual structure contributing more than 7% and most less than 1%. Similar NRT results are obtained for the $(\text{CH}_3)_2\text{S}-\text{CH}_2$ ylide, with single- and double-bond contributions of 41 and 28%, respectively.

The NRT analysis of sulfur ylides compares favorably with the sharing analysis reported by Mitrasinovic.¹⁴ In that work, the sharing indices between the sulfur and carbon basins in the sulfur ylides were determined to be 1.23 and 1.24 in $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$, respectively. For comparison, the sulfur-carbon sharing indices for CH_3SH and H_2CS were calculated to be 0.93 and 1.66, respectively; thus, the sharing analysis also predicts the C-S ylide bond to be intermediate between a single and double bond, though the bond order is not given explicitly.

4. Conclusions

Through the use of density functional and ab initio methods, in conjunction with the NBO and NRT techniques, a detailed quantitative analysis of the structure and bonding of sulfur ylides has been presented. Structurally, the sulfur ylides $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$ are found to possess C-S bonds only slightly longer than that of a typical C-S double bond. Exploration of the charge distribution of the ylides using natural population analysis provides an explanation of the unusually short ylide bonds. Because of a significant amount of charge transfer (around 0.6 e) from the sulfide to the carbene, the sulfur and carbene carbon atoms of the ylides are found to be highly oppositely charged. Electrostatic attraction between the oppositely charged sulfur and carbon atoms leads to a shorter than expected bond distance, close to that of a double bond.

The origin of the large torsional barrier in sulfur ylides relative to other types of ylides has been explained using NBO analysis. The $n \rightarrow \sigma^*$ stabilization arising from donation of electron density from the carbon lone pair orbital into S-H or S-C antibonding orbitals leads to the larger than expected torsional barriers. This stabilization of the sulfur ylides is consistent with delocalization of electron density over the carbon atom of the carbene, the sulfur atom, and the hydrogen or carbon atoms attached directly to the sulfur atom of the sulfide.¹⁴

Finally, NRT analysis provides a quantitative description of the bond order and resonance contributions to the bonding of the sulfur ylides. The calculated NRT bond orders of the sulfur ylides fall in the range 1.4–1.5, intermediate between single and double bonds. Furthermore, NRT analysis indicates that the singly bonded resonance structure is the leading contributor by more than a factor of 2 over the doubly bonded resonance structure.

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Supporting Information Available: Cartesian coordinates, electronic energies, and vibrational zero-point energies for each

level of theory and basis set are available for the sulfur ylides in the Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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