

methods in this area is probably some way off, but the methods described here may well provide useful techniques for extending the range of applicability of the free energy perturbation and related methods.

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## Ab Initio Molecular Orbital Studies of the Rotational Barriers and the <sup>33</sup>S and <sup>13</sup>C Chemical Shieldings for Dimethyl Disulfide

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**Abstract:** A series of ab initio molecular orbital calculations were carried out for dimethyl disulfide as a model for the disulfide bridges in proteins and peptides. The potential energy profile for rotation around the S-S bond was obtained at the HF/6-31G\* level with full geometry optimization. Cis- and trans-barrier heights were estimated to be 11.40 and 6.27 kcal/mol, respectively, on the basis of fourth-order Møller-Plesset perturbation theory and 6-311G\*\* basis sets. Calculations of the torsion angle dependence of the isotropic <sup>33</sup>S and <sup>13</sup>C NMR shieldings were based on the method of individual gauge for localized orbitals (IGLO). These are of interest for NMR studies of the disulfide bond in peptides and proteins. The minimum in the plot of <sup>13</sup>C shielding as a function of torsion angle occurs for a C1-S1-S2-C2 angle close to 110°, which is an optimum arrangement for lone pair back-bonding. An analysis of the paramagnetic bond contributions to the <sup>13</sup>C shielding at C1, for example, shows that the conformational dependence is dominated by the paramagnetic contributions to the C1-H1 bond, which points away from a lone pair on S2.

### Introduction

The disulfide bridge is one of the two major covalent linkages between amino acids in polypeptides and proteins.<sup>1</sup> It has been known that disulfides in protein structures enhance the overall stability of some particular conformations.<sup>2</sup> In recent years, the use of conformational constraints has gained general attention in peptide synthesis.<sup>3</sup> In particular, disulfide formation has been used to limit the number of conformational states and to force  $\beta$ -turn-type conformations. Following current trends, which make use of molecular mechanics and molecular dynamics to study conformational property of peptides and proteins, refinement of force fields demands accurate experimental data, or high-level ab initio quantum chemical calculations for small but representative fragments of peptides and proteins.

In many experimental and theoretical studies dimethyl disulfide has been a model for the disulfide linkages in proteins or peptides.<sup>4</sup> Previous theoretical studies of dimethyl disulfide gave two energy barriers for rotation about the S-S bond. The trans-barrier is lower than the cis-barrier. The barriers create two minimum-energy conformations with C-S-S-C torsional angles near +90° or -90°. Although the geometry of (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> was determined experimentally by microwave spectroscopy and by electron dif-

Table I. Ab Initio Calculations of Torsional Barriers for Dimethyl Disulfide

methods	dihedral angles, deg	energy barriers, kcal/mol	
		cis	trans
STO-3G (rigid rotor) <sup>a</sup>	90	18.0	4.4
STO-3G* (rigid rotor) <sup>a</sup>	90	24.1	12.7
MB (rigid rotor) <sup>b,c</sup>	82.84	13.11	10.39
DZ (rigid rotor) <sup>c,d</sup>	86.23	16.03	9.16
STO-3G (opt) <sup>e</sup>	89.5	15.62	5.05
HF/4-31G//HF/STO-3G <sup>e</sup>	89.5	18.47	6.04
STO-3G <sup>f</sup>		12.68	6.27
DH+d <sup>f</sup>		16.49	8.00
HF/3-21G*//HF/3-21G* <sup>g</sup>	88.4 (opt)	11.97	5.69
HF/6-31G*//6-31G* <sup>h</sup>	87.29 (opt)	11.36	5.72
HF/4-31G*//HF4-31G* <sup>i</sup>	90 (fixed)	11.5	5.7
CI/4-31G*//HF/4-31G* <sup>i</sup>	90 (fixed)	9.4	6.0

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fraction methods, the only known experimental value corresponding to an "effective rotational barrier" around the S-S bond is 6.8 kcal/mol from gas-phase thermodynamic studies.<sup>5</sup> This value has been taken as the trans-barrier height. There appears

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**Table II.** Geometries and Energies of Dimethyl Disulfide Optimized with HF/6-31G\*

CSSC, deg	SS, Å	CS, Å	SSC, deg	$E_{\text{rel}}$ , kcal/mol
0.0	2.111	1.812	106.3	11.27
30.0	2.091	1.811	105.2	7.62
60.0	2.061	1.814	103.8	1.96
87.4	2.053	1.815	103.1	0.00 <sup>a</sup>
120.0	2.067	1.815	101.7	2.03
150.0	2.084	1.812	99.4	4.61
180.0	2.090	1.811	98.2	5.50

<sup>a</sup>The total energy at this point is  $-874.247\ 655$  au.

not to be an experimental value for the cis-barrier height even though this is very important in the refinement of the molecular mechanics force field. A similar situation occurred for the cis-barrier in *n*-butane.<sup>6</sup>

Few ab initio calculations of dimethyl disulfide energy barriers made use of large basis sets and full geometry optimization (see Table I). Literature values for the cis- and trans-barriers, which range from 9.4 to 24.1 kcal/mol and from 5.72 to 12.7 kcal/mol, respectively, show some convergence with improved quality of the computations. Calculated results reported here make use of larger basis sets, fully optimized geometries, and electron correlation effects. These are all important factors for good quality calculations of energy barrier heights.<sup>6,7</sup> In the absence of accurate experimental data, the intent was to produce more reliable torsional barriers for  $(\text{CH}_3)_2\text{S}_2$  for refinement of molecular mechanics force fields.

Several physical properties have been used to study the conformations around the disulfide bridge. These include optical rotation,<sup>8</sup> vibrational frequencies,<sup>9</sup> and ionization potentials.<sup>10</sup> Another possibility for experimental investigation of the torsion angle dependence is presented here. A series of ab initio IGLO MO calculations were performed to explore the conformational dependence of the <sup>13</sup>C and <sup>33</sup>S isotropic chemical shieldings for dimethyl disulfide.

### Computational Methods

Ab initio molecular orbital calculations<sup>6</sup> were performed either with Gaussian 88<sup>11</sup> or Gaussian 90<sup>12</sup> codes on Convex 220 or Cray Y-MP computers. Initially, a set of optimized geometries was obtained at different dihedral angles around the disulfide bond at the 6-31G\* level (a split valence basis set with d-orbitals on carbon and sulfur atoms) using GAMESS.<sup>13</sup> The resulting geometries were used as input for further geometry optimization and for the chemical shielding calculations. Energies were analyzed in terms of a truncated Fourier-type expansion of the potential function<sup>14</sup>

$$V(\phi) = (1/2)V_1(1 - \cos \phi) + (1/2)V_2(1 - \cos 2\phi) + (1/2)V_3(1 - \cos 3\phi) \quad (1)$$

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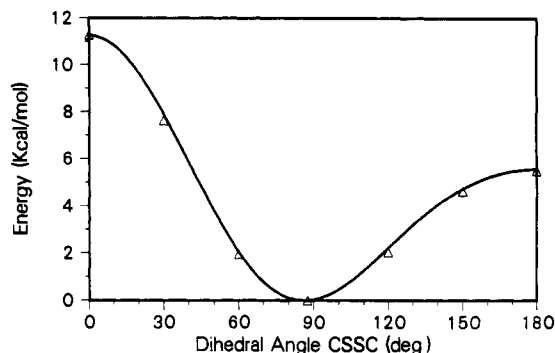
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**Figure 1.** Relative energies (kcal/mol) for dimethyl disulfide plotted as a function of the C–S–S–C dihedral angle  $\phi$ . The open triangles denote the calculated data points and the solid curve is based on the linear regression result.

where the coefficients  $V_i$  have been interpreted in terms of electronic and steric effects.<sup>14,15</sup> Geometries were additionally optimized by assuming  $C_2$  symmetry at the MP2/6-31G\*\* level, e.g., the second-order Møller–Plesset perturbation theory with the standard split valence basis set and a set of polarization functions on all atoms. The geometry was fully optimized at the energy minimum point. The other two points were established by fixing the dihedral angles of C–S–S–C at 0 or 180°, while all other parameters were optimized (see Table II).

To investigate the effects of larger basis sets and electron correlation on the torsional barriers, standard split valence and triple split valence basis sets with polarization functions 6-31G\*\* and 6-311G\*\*, respectively, were used in conjunction with electron correlation treatments through configuration interaction (CI)<sup>16</sup> with single and double excitations (CISD) and the Møller–Plesset (MP)<sup>17</sup> perturbation theory up to fourth-order (MP4). The lowest total energies obtained with different basis sets and CI and MP treatments are included in Table III. Relative energies corresponding to the three conformations are tabulated in Table IV. In these tables CISD(Q) denotes the CISD energy, which includes contributions from unlinked quadruple excitations as estimated from Davidson's formula.<sup>18</sup> These single-point energy calculations made use of the previously described optimized geometries at the MP2/6-31G\*\* level (see Table V).

All chemical shielding calculations in this study were based on the IGLO (individual gauge for localized orbital) formulation of Kutzelnigg and Schindler.<sup>19</sup> Problems associated with origin dependence usually found in coupled Hartree–Fock (CHF) shielding computations, arising from a common origin and an incomplete basis set,<sup>20</sup> are less severe in the IGLO method. In this method localized MO's associated with inner shells, bonding orbitals, and lone pairs have unique origins for the calculation of diamagnetic and paramagnetic terms. In a recent study of the conformational dependence of <sup>13</sup>C chemical shifts of hydrocarbons,<sup>21</sup> it was shown that double- $\zeta$  quality basis sets give reasonable results for most situations. For dimethyl disulfide, however, shielding calculations at the double- $\zeta$  level are not adequate even to predict conformational trends. Difficulties with shielding calculations with a small basis set on sulfur have been noted previously.<sup>22</sup> Calculations for  $(\text{CH}_3)_2\text{S}_2$  were

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Table III. Total Energies of Dimethyl Disulfide<sup>a</sup>

basis set	HF	CISD	CISD(Q)	MP2	MP3	MP4
6-31G**	-874.257 107			-874.801 322	-874.849 869	-874.873 644
6-311G**	-874.315 927	-874.843 291	-874.923 449	-874.887 300	-874.935 542	-874.962 656

<sup>a</sup> Based on the lowest energy geometry optimized at MP2/6-31G\*\*. All values in au's.

Table IV. Relative Energies (kcal/mol) of Dimethyl Disulfide at Three Conformations

CSSC, deg	HF	CISD	CISD(Q)	MP2	MP3	MP4
6-31G** Basis Set						
84.8	0.00			0.00	0.00	0.00
0.0	11.09			11.48	10.97	11.10
180.0	5.47			6.19	5.90	6.14
6-311G** Basis Set						
84.8	0.00	0.00	0.00	0.00	0.00	0.00
0.0	10.86	11.41	11.21	11.80	11.25	11.40
180.0	5.23	5.94	5.97	6.33	6.45	6.27

Table V. MP2/6-31G\*\* Optimized and Experimental Geometries of Dimethyl Disulfide

geometrical parameters <sup>a</sup>	optimized values			microwave spectroscopy <sup>b</sup>	electron diffraction <sup>c</sup>
	lengths, Å	angles, deg			
CSSC	84.8	0.0	180.0	84.7	83.9 ± 0.09
SS	2.054	2.122	2.098	2.038	2.022 ± 0.003
CS	1.810	1.804	1.804	1.810	1.806 ± 0.002
CSS	102.0	105.2	96.7	102.8	104.1 ± 0.3
CH <sub>1</sub>	1.088	1.088	1.086	1.097	1.090 ± 0.007
CH <sub>2</sub>	1.085	1.085	1.086		
CH <sub>3</sub>	1.086	1.085	1.086		
SCH <sub>1</sub>	106.7	104.3	106.5	108.9	106.5 ± 1.0
SCH <sub>2</sub>	110.8	112.6	111.2		
SCH <sub>3</sub>	111.5	112.6	111.2		
SSCH <sub>1</sub>	177.8	180.0	180.0		
SSCH <sub>2</sub>	59.0	62.8	61.4		
SSCH <sub>3</sub>	-63.6	-62.8	-61.4		

<sup>a</sup> Bond lengths, internal angles, and dihedral angles are specified by two-, three-, or four-atom labels. Subscripts 1, 2, and 3 are used to specify parameters involving three different hydrogens. <sup>b</sup> Reference 4a. <sup>c</sup> Reference 4b.

based on a (9,5/5) Huzinaga set<sup>23</sup> contracted to a triple- $\zeta$  (51111;311/311) set with d- and p-type polarization functions on C (exponent 0.7) and hydrogen (exponent 1.0), respectively. For sulfur a (10,6) Huzinaga set<sup>23</sup> contracted to a triple- $\zeta$  (51111;3111) set was used with the d-type orbital exponent 0.5. Geometries optimized at the HF/6-31G\* level were used in the shielding calculations.

## Results and Discussion

**1. Geometries.** Optimized results at the HF/6-31G\* level in Table II are similar to those reported by Aida et al.<sup>24</sup> Bond lengths, internal angles, and dihedral angles are specified by two-, three-, or four-atom labels. The dependence of the S-S bond length and S-S-C bond angles on the dihedral angle around the S-S bond reflects the change of S-S bond strength or force constant.<sup>9,24</sup> The MP2/6-31G\*\* optimized geometry is also given in Table V. A significant improvement over Hartree-Fock level optimization is the decrease of the dihedral angle around the S-S bond from 87.4° (HF/6-31G\*) to 84.8° (MP2/6-31G\*\*). The latter value is in good agreement with the experimental (microwave) value of 84.7° in Table V. The only significant difference (0.02 Å) between the optimized and the experimental geometries occurs for the S-S bond length. This difference is comparable to the difference between microwave spectroscopic and electron diffraction data in Table V and a similar disparity occurs for H<sub>2</sub>S<sub>2</sub>.<sup>25</sup> Moreover, the microwave spectroscopic study<sup>4a</sup> assumed

that methyl groups are exactly staggered whereas these optimized results here indicate that the methyl groups are twisted from the staggered conformation, in agreement with the gas-phase electron diffraction results.<sup>4b</sup>

**2. Torsional Energy Barriers.** Calculated relative energies at 30° intervals of the dihedral angle are given in Table II (HF/6-31G\*). These exhibit a qualitatively correct (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> potential surface, which is characterized by an energy minimum near 85°. These data are also plotted (triangles) in Figure 1 as a function of the dihedral angle  $\phi$ . Cis- and trans-barrier heights are close to those reported by Aida et al.<sup>24</sup> After an analysis in terms of a Fourier-type expansion of the potential function,<sup>14,15</sup> a representation of the energy profile was obtained in the form of eq 1 with  $V_1 = -3.68$ ,  $V_2 = -8.37$ , and  $V_3 = -2.01$  kcal/mol. The solid line in Figure 1 is a plot of eq 1 with these values of  $V_i$ . The most important term here is the 2-fold term  $V_2$ , which is the predominant term for a disulfide bridge to adopt a skew conformation.<sup>14</sup> The  $V_1$  term, which is associated with dipole-dipole interactions, and to a smaller extent the  $V_3$  term, which involves bond repulsion terms, make the (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> cis-barrier higher than the trans-barrier.<sup>14,15</sup> This analysis is consistent with previous MO studies on disulfides.<sup>24,26</sup>

Since the (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> potential curve in Figure 1 is relatively flat at the bottom of the well, there is little energy penalty for distorting a disulfide bond from its lowest energy dihedral angle within this range. As little as 2 kcal/mol can cause the rotation of the C-S-S-C dihedral angle from 60° to 120°. This suggests that the disulfide bridge offers considerable flexibility for peptide and protein conformations and it is consistent with the fact that in peptides and proteins those disulfide bridges that are not severely constrained have dihedral angles in the range 60–120°.<sup>27</sup>

In contrast to the *n*-butane situation,<sup>6,28</sup> electron correlation effects increase the dimethyl disulfide barrier heights (see Table IV). These calculations show an interesting trend for (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>: within the Hartree-Fock limit, larger basis sets seem to give the lower barrier heights, but when using the same basis set (especially at the triple- $\zeta$  level), CI or MP results tend to increase the barrier heights by 0.6–1.0 kcal/mol. These results are different from the recent observation by Loos<sup>29</sup> wherein the cis-barrier height was decreased 2.1 kcal/mol upon inclusion of electron correlation effects through CI/4-31G\*. It seems likely that the differences arise because a different geometry was used for the minimum-energy conformation (the dihedral angle of the S-S bond was fixed at 90°) and the author used a smaller basis set. Viewing the experimental barrier from gas-phase thermodynamic properties as an "effective barrier" for internal rotation, at elevated temperatures the value of 6.8 kcal/mol may correspond to a weighted average of cis- and trans-barriers.<sup>5</sup> Calculations reported here, which do not include zero-point energy corrections, suggest that the cis and trans torsional barriers are 11.40 ± 0.20 and 6.27 ± 0.20 kcal/mol, respectively. Recent experimental NMR relaxation data for cyclic tetrapeptides<sup>30</sup> indicate values of 10.8 ± 0.2 kcal/mol for the disulfide cis-barrier. In the NMR study of 1,2-dithiane<sup>31</sup> where the six-membered ring precludes the pos-

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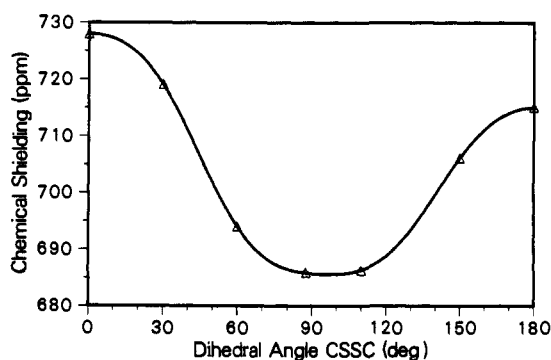
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**Table VI.** IGLO Results for  $^{33}\text{S}$  and  $^{13}\text{C}$  Chemical Shieldings of Dimethyl Disulfide<sup>a</sup>

dihedral angle of CSSC, deg	chemical shielding and chemical shift, ppm			
	$\sigma(^{33}\text{S})$	$\delta(^{33}\text{S})^c$	$\sigma(^{13}\text{C})$	$\delta(^{13}\text{C})^d$
0.0	728.0	-84.4	199.1	14.8
30.0	719.1	-75.5	197.7	16.2
60.0	694.0	-50.4	195.5	18.4
87.4 <sup>b</sup>	685.9	-42.3	193.1	20.8
110.0	686.3	-42.7	191.5	22.4
150.0	706.1	-62.5	194.6	19.4
180.0	715.1	-71.5	196.4	17.5

<sup>a</sup>Geometry based on HF/6-31G\* optimization. Basis sets for shielding calculations are described in the text. <sup>b</sup>The total energy at this point is -874.006314 au. <sup>c</sup>The chemical shifts are relative to carbon disulfide ( $\sigma = 643.6$  ppm). The shielding calculation made use of the same basis sets and the optimized geometry at the HF/6-31G\* level. <sup>d</sup>The chemical shifts are relative to TMS, which is 2.3 ppm downfield from methane ( $\sigma = 216.2$  ppm). The shielding calculation made use of the same basis sets and the optimized geometry at the HF/6-31G\* level.



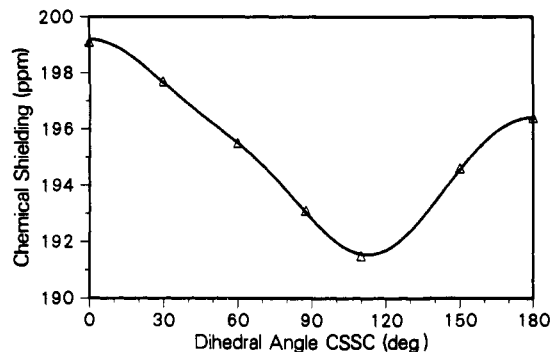
**Figure 2.** Calculated  $^{33}\text{S}$  isotropic shielding (ppm) for dimethyl disulfide plotted as a function of the dihedral angle  $\phi$ . The open triangles denote the calculated points and the solid line is based on the linear regression results from eq 2.

sibility for trans arrangements, it was concluded that the disulfide cis-barrier is 11.6 kcal/mol. In comparison, an NMR study of the rotational barrier in molecules such as  $\text{PhCH}_2\text{SSC}(\text{CH}_3)_3$ , for example, shows a value of  $6.8 \pm 0.7$  kcal/mol.<sup>32</sup> Since the large bulky groups would substantially raise the cis-barrier heights, this value could represent an upper limit for the trans-barrier height in dimethyl disulfide.

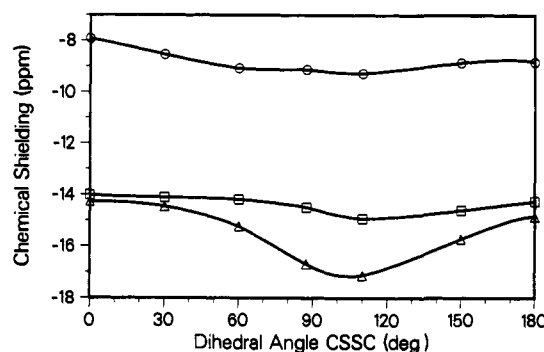
**3. Chemical Shielding. (a) Conformational Dependence of the Isotropic  $^{33}\text{S}$  Shielding in  $(\text{CH}_3)_2\text{S}_2$ .** Entered in Table VI are the calculated IGLO  $^{13}\text{C}$  and  $^{33}\text{S}$  chemical shielding results at  $30^\circ$  intervals of the C-S-S-C dihedral angle  $\phi$ . These data are also plotted (triangles) in Figure 2 as a function of the C-S-S-C torsional angle in the range  $0-180^\circ$ . From the linear regression analysis of the results in Table VI, it can be seen that the conformational dependencies are well represented by the Fourier expansion

$$\sigma(^{33}\text{S}) = 6.8 \cos \phi + 18.8 \cos 2\phi + 0.4 \cos 3\phi + 1.1 \cos 4\phi - 0.7 \cos 5\phi - 1.1 \cos 6\phi + 702.5 \text{ ppm} \quad (2)$$

with a standard deviation of less than 0.1 ppm. The solid curve in Figure 2 is a plot of the shielding based on eq 2. There is a substantial chemical shift range of almost 50 ppm in Figure 2, but  $^{33}\text{S}$  resonances in these compounds might be very broad.<sup>33</sup> The magnitudes of computed  $^{33}\text{S}$  isotropic chemical shielding values in Table VI are consistent with IGLO results with comparable basis sets. The experimental value of the  $^{33}\text{S}$  chemical shift for  $(\text{CH}_3)_2\text{S}_2$



**Figure 3.** Calculated  $^{13}\text{C}$  isotropic shielding (ppm) for dimethyl disulfide plotted as a function of the dihedral angle  $\phi$ . The open triangles denote the calculated points and the solid line is based on the linear regression results from eq 3.



**Figure 4.** Angular dependence of the calculated paramagnetic bond contributions (PBC) to the  $^{13}\text{C}$  shielding in dimethyl disulfide: (O) C1-S1; (□) average for C1-H2 and C1-H3; (Δ) C1-H1.

seems not to have been reported.<sup>33</sup>

**(b) Conformational Dependence of the Isotropic  $^{13}\text{C}$  Shielding in  $(\text{CH}_3)_2\text{S}_2$ .** Entered in Table VI are the IGLO results for the isotropic  $^{13}\text{C}$  chemical shielding in  $(\text{CH}_3)_2\text{S}_2$  for representative torsional angles  $\phi$ . These are plotted (triangles) in Figure 3 as a function of the dihedral angles in the range  $0-180^\circ$ . Analysis of the chemical shieldings in terms of a truncated Fourier expansion gives the following equation:

$$\sigma(^{13}\text{C}) = 2.0 \cos \phi + 2.5 \cos 2\phi - 0.8 \cos 3\phi + 0.3 \cos 4\phi + 0.2 \cos 5\phi + 195.0 \text{ ppm} \quad (3)$$

with a standard deviation of less than 0.1 ppm. The  $^{13}\text{C}$  shielding results from eq 3 are plotted (solid curve) in Figure 3 as a function of dihedral angle.

For dimethyl disulfide at the equilibrium geometry the calculated (gas-phase)  $^{13}\text{C}$  NMR  $\text{CH}_3$  chemical shift is 22.4 ppm. This value is in fortuitously good agreement with the experimental (solution) value of 22.2 ppm measured in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as reference.<sup>34</sup> The calculated value was first referenced to the IGLO shielding result (216.2 ppm) for methane (geometry optimized at the 6-31G\*\* level) obtained with the same basis set and then referenced to TMS by means of the experimental (-2.3 ppm) chemical shift of  $\text{CH}_4$ .<sup>35</sup> It is possible that the modest basis sets used here are adequate to reproduce conformational chemical shift trends around the disulfide bond. Even though the  $^{13}\text{C}$  chemical shifts exhibit a range of more than 7 ppm in Figure 3, there does not yet appear to be unambiguous conformational data for comparison. In studies of cystine residues of protected and unprotected oxytocin intermediates, it has been proposed<sup>36</sup> that the observed  $^{13}\text{C}$  chemical shifts arise from var-

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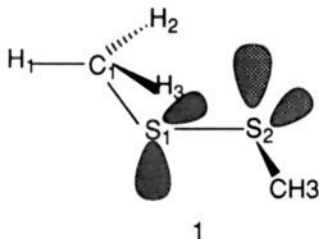
(34) The Sadtler Standard  $^{13}\text{C}$  NMR Spectra, Sadtler Research Lab. Inc., 1977; Vol. 16, p 3008c.

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iations of the C-S-S-C dihedral angle associated with amino group charge density changes.

From the IGLO studies of  $^{13}\text{C}$  shielding in hydrocarbons<sup>19,21</sup> it has been shown that the most important changes in the total shielding arise from paramagnetic contributions to the localized MO's. To study the origin of the angularly dependent substituent effects, the individual paramagnetic bond contributions (PBC) to the  $(\text{CH}_3)_2\text{S}_2$   $^{13}\text{C}$  shielding from the four localized bonds (C1-S1, C1-H1, C1-H2, and C1-H3 in **1**) on carbon were fit



in the least-squares sense to a truncated Fourier series. These PBC are plotted as a function of the dihedral angle  $\phi$  in Figure 4. The paramagnetic bond contributions associated with the C1-S1 bond, which are plotted (open circles) in Figure 4, vary by somewhat more than 1 ppm over the whole range of dihedral angles. The average of the PBC from the C1-H2 and C1-H3 bonds (open squares in Figure 4) is used since this has a periodicity of  $180^\circ$ . These contributions vary by no more than 1 ppm over the whole range. The angularly dependent changes involving the C1-H1 bond (triangles in Figure 4) are most important. The conformational dependence of the C1 methyl shielding in **1** is almost entirely attributable to the paramagnetic bond contributions for the C1-H1 bond, which points away from a lone pair on S2.

Radom et al. discussed the significance of the various  $V_i$  terms in eq 1 for the conformational dependence of the energies.<sup>14</sup> Although there is no obvious reason that the torsional features of the shielding should parallel the energies, in some cases they

are similar. For example, the calculated isotropic  $^{13}\text{C}$  shielding in ethane is very accurately described by the 3-fold term.<sup>21</sup> This term corresponds to interactions between the C-H bonds, which energetically favor staggered conformations. From eq 3 it can be seen that the  $^{13}\text{C}$  isotropic shielding has contributions from the 2-fold term that are slightly larger than those from the 1-fold term. Radom et al.<sup>14</sup> analyzed the 1-fold term as arising from local dipole interactions at the two ends of the molecule. The 2-fold term, which is ascribed to interactions (back-donation) between lone pairs and bond pairs, is the dominant factor leading to the skew conformation of  $(\text{CH}_3)_2\text{S}_2$ . The back-donation of an S2 lone pairs to a bond pair on C1 might explain why paramagnetic bond contributions from the C1-H1 bond dominate the conformational features of the isotropic  $^{13}\text{C}$  shielding in  $(\text{CH}_3)_2\text{S}_2$ .

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**Registry No.** dimethyl disulfide, 624-92-0.

**Supplementary Material Available:** Tables of optimized (HF/6-31G\* with GAMESS) coordinates for dimethyl disulfide for eight values of the dihedral angle and optimized geometries at the MP2/6-31G\*\* level using the Gaussian 88 codes for dihedral angles of  $0^\circ$ ,  $84.8^\circ$ , and  $180^\circ$  (5 pages). Ordering information is given on any current masthead page.

## Mechanistic, Structural, and Vibrational Aspects of the Dimerization of Silaethylene

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**Abstract:** The dimerization of silaethylene to form 1,3-disilacyclobutane (1,3-DSCB) and 1,2-disilacyclobutane (1,2-DSCB) is studied using ab initio quantum mechanical techniques. The dimerization reaction leading to 1,3-DSCB is predicted to proceed through a concerted 2S + 2S mechanism due to a relaxation of the Woodward-Hoffmann rules for this case. With use of a double- $\zeta$  basis set augmented with polarization functions on C and Si (DZ + d), at the single and double excitation coupled cluster (CCSD) level of theory, this reaction is predicted to be exothermic by 79.1 kcal/mol, and to have a barrier height of 5.2 kcal/mol. 1,2-DSCB is predicted to lie 19.8 kcal/mol higher in energy than 1,3-DSCB at the DZ + d self-consistent field (SCF) level of theory, and the dimerization reaction leading to 1,2-DSCB is predicted to proceed through a two-step mechanism involving a diradical intermediate.

### Introduction

For more than 2 decades it has been known that silicon can and does form double bonds with carbon.<sup>1</sup> It was not until 1979, however, that the synthesis of the first of a family of relatively

stable silenes, with the general formula  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$ , was reported by Brook et al.<sup>2</sup> Unlike previously known unstable silenes which dimerize in a head-to-tail fashion to produce 1,3-disilacyclobutanes (1,3-DSCBs),<sup>3</sup> most members of this family

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