



Hypercoordination to a saturated carbon atom

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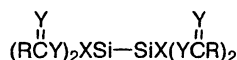
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Abstract—Recently, the first heptacoordinate disilane [(MesCS₂)₂MeSi]₂ **1** was synthesized and shown to have a unique structure by X-ray analysis. Each of the silicon atoms is surrounded by three nonbonded thiobenzoylthio groups. We theoretically investigated the origins of the unusual geometry of **1** containing multiple hypercoordinations. The model compound [(HCS₂)₂MeSi]₂ **2a** shows both the H-C–Si–Si eclipsed conformation and the C–Si–Si–C eclipsed conformation. The dihedral angle of H–C–Si–Si is calculated to be 24.6° at the RHF/6-31G* level (25.7° at the RHF/LANL2DZ+p level). Each of the carbon atoms of the methyl groups is also surrounded by three nonbonded thioformylthio groups. After the bond model analyses, we found that hypercoordination to the saturated carbon atom is essential for this unique geometry, as confirmed by scrutinizing the X-ray data of **1**. © 2002 Elsevier Science Ltd. All rights reserved.

There is growing interest in hypercoordination.^{1–3} Although several papers have reported hypercoordination to a saturated third-row atom,² none have described that to a saturated second-row atom.

Recently, the first heptacoordinate disilane [(MesCS₂)₂MeSi]₂ **1** was synthesized and shown to have a unique structure by X-ray analysis.⁴ Each of the silicon atoms is surrounded by three nonbonded thiobenzoylthio groups. The thiocarbonyl sulfur atoms are located at distances of 3.049, 3.438 and 3.461 Å, which are shorter than the sum of the van der Waals radii of silicon and sulfur (3.90 Å).⁵ These results suggested hypercoordination of the thiocarbonyl sulfur atoms to a silicon atom. On the other hand, one of the thiocarbonyl sulfur atoms is close to both of the silicon atoms, suggesting hypercoordination of the sulfur atom. We theoretically investigated the origins of the unusual geometry of **1** containing multiple hypercoordinations. We theoretically found hypercoordination to a saturated carbon atom, a second-row atom, and confirmed this by scrutinizing X-ray data.



- 1:** X = Me; Y = S; R = 2,4,6-trimethylphenyl
2: X = Me; Y = S; R = H
3: X = H; Y = S; R = H

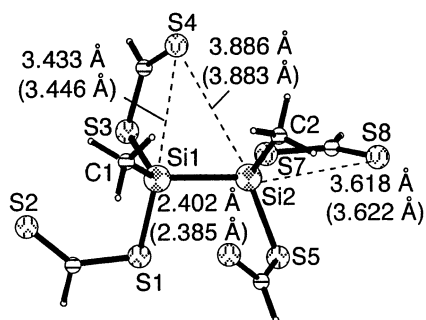
We used the model compound [(HC(=S)S)₂MeSi]₂ **2**, in which all of the mesityl groups are replaced by hydrogen atoms. The geometry optimization at the RHF/6-31G* level⁶ gives structure **2a** (Fig. 1), similar to that observed for **1**. The three nonbonded distances of S··Si are 3.433, 3.618 and 3.886 Å. The dihedral angles of 19.6° for S–Si–Si–S, and 24.9° for C–Si–Si–C are comparable to the values⁴ (12.4° and 14.5° for S–Si–Si–S; 19.9° for C–Si–Si–C) observed for **1**. These results show that **2** is a good model for investigating the unusual geometry of **1**.

To our surprise, the C–H bonds of the methyl groups on the Si atoms in **2a** were also closely eclipsed with the Si–Si bond in the optimized geometry. The calculated dihedral angle of H–C–Si–Si in **2a** is 24.6° at the RHF/6-31G* level and 25.7° at the RHF/LANL2DZ+p level (Fig. 2). We calculated the change in energy with rotation of the methyl groups about the Si–C bonds (Fig. 3), and found that **2a** is an exclusive conformer about the Si–C bonds.

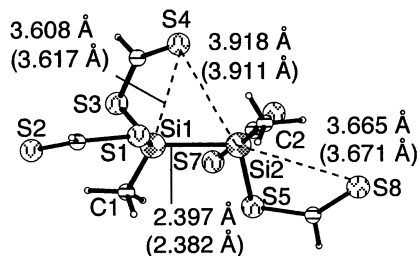
We initially focused our attention on the eclipsed conformation about the Si–Si bond. The bond model analyses^{7–9} were performed at the RHF/LANL2DZ level to investigate this unique structure. We used the interbond energy (IBE)⁹ to estimate the interactions between the bonds and between the bond orbitals. The results (Table 1) supported the triple hypercoordination of thiocarbonyl sulfur atoms to a silicon atom and the

Keywords: hypercoordination; disilane; dithiocarboxylate.

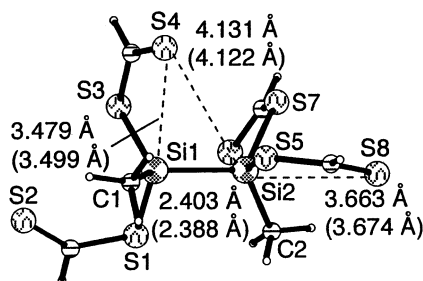
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2a ($\Delta E = 0.0$ (0.0) kcal·mol⁻¹)



2b ($\Delta E = 1.1$ (1.7) kcal·mol⁻¹)



2c ($\Delta E = 2.0$ (2.2) kcal·mol⁻¹)

Figure 1. The optimized structures and the relative energies of **2** at the RHF/6-31G* level (ZPE corrected, RHF/LANL2DZ+p level in parentheses).

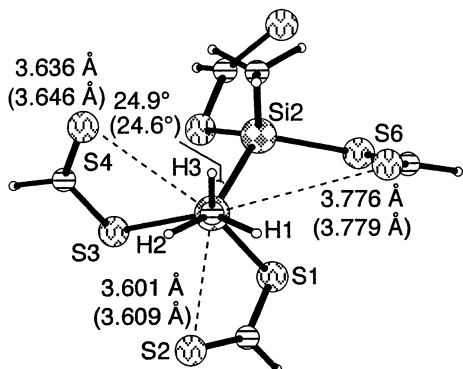


Figure 2. The closely eclipsed conformation about the Si-C bond in **2a**. The S...C distances calculated at the RHF/6-31G* level (RHF/LANL2DZ+p level in parentheses).

double hypercoordination of a sulfur atom to the silicon atoms. The strong interactions between the lone pair on the thiocarbonyl sulfur atoms and the corre-

sponding σ_{SiS}^* orbitals produce large stabilization ($\text{IBE}(n_{\text{S}}, \sigma_{\text{SiS}}^*) = -0.0821, -0.0289$ and -0.0366 a.u.). The corresponding interactions between the occupied orbitals of the lone pair and the σ_{SiS} bond are weakly repulsive ($\text{IBE}(n_{\text{S}}, \sigma_{\text{SiS}}) = 0.0077$ and 0.0072 a.u.), or slightly bonding ($\text{IBE}(n_{\text{S}}, \sigma_{\text{SiSi}}) = -0.0006$ a.u.). Net stabilization ($\text{IBE}(n_{\text{S}}, \sigma_{\text{SiS}}^*) + \text{IBE}(n_{\text{S}}, \sigma_{\text{SiS}}) < 0$) results from the interactions of lone pairs on S with the σ_{SiS} bonds, in agreement with the hypercoordination.

We identified other conformers **2b** and **2c** about the Si-Si bond. The thiocarbonyl sulfur atom of a thiocarbonyl group is missing at the backside of the Si-S bond of the geminal thioformylthio group in **2b**. No stabilization is expected from the S...Si-S hypercoordinations in the geminal groups. On the other hand, the missing hypercoordinations between the vicinal thioformylthio groups in **2c** are expected to lessen the stability. In fact, the conformers **2b** and **2c** are higher in energy than **2a** by 1.1 kcal mol⁻¹ at the RHF/6-31G* level (1.7 kcal mol⁻¹ at the RHF/LANL2DZ+p level) and by 2.0 kcal mol⁻¹ at the RHF/6-31G* level (2.2 kcal mol⁻¹ at the RHF/LANL2DZ+p level). These results suggest that both geminal and vicinal hypercoordinations play significant roles in stabilizing the observed structure of **1**.

We next turned our attention to the conformation about the Si-C bond. We examined the eclipsed conformation of the C-H bond of the methyl group and the Si-Si bond. The bond model analysis showed surprising hypercoordination of the thiocarbonyl sulfur atoms to the methyl carbon atoms. The interactions of the C-H bonds with the lone pairs of the thiocarbonyl sulfur at the backsides of the methyl CH bonds produce considerable net stabilizations ($\Sigma \text{IBE}(n_{\text{S}}, \text{CH}) = -0.0200, -0.0135,$ and -0.0084 a.u.) (Table 2). The distances from the carbon atom to the three sulfurs are C1...S2 3.601 Å, C1...S4 3.636 Å and C1...S6 3.776 Å at the RHF/6-31G* level (3.609, 3.646 and 3.779 Å at the RHF/LANL2DZ+p level) and the three S...C-H angles are close to 180° ($\angle \text{S2}\cdots\text{C1-H3}$ 172.3°, $\angle \text{S4}\cdots\text{C1-H1}$ 171.6° and $\angle \text{S6}\cdots\text{C1-H2}$ 166.3° at the RHF/6-31G* level; 171.1°, 170.2° and 165.6° at the RHF/LANL2DZ+p level, respectively). The sulfur atoms are located where the lone pair orbitals effectively interact with the backside lobes of the σ_{CH}^* orbitals. Thus, we conclude that this CH-SiSi eclipsed conformation results from hypercoordination to a saturated carbon atom!

When we replaced the methyl groups by hydrogens to eliminate the hypercoordination of the sulfurs to the methyl carbon atoms, the preference for **3a**, which corresponds to the most stable conformer **2a**, with respect to the conformer **3b** is dramatically reduced to 0.3 kcal mol⁻¹ at the RHF/6-31G* level (0.3 kcal mol⁻¹ at the RHF/LANL2DZ+p level). The preference for **3a** relative to **3c** is only 0.6 kcal mol⁻¹ at the RHF/6-31G* level (0.8 kcal mol⁻¹ at the RHF/LANL2DZ+p level). Hypercoordination of the thiocarbonyl sulfurs to the methyl carbon atoms should contribute to the observed structure of **1**.¹⁰

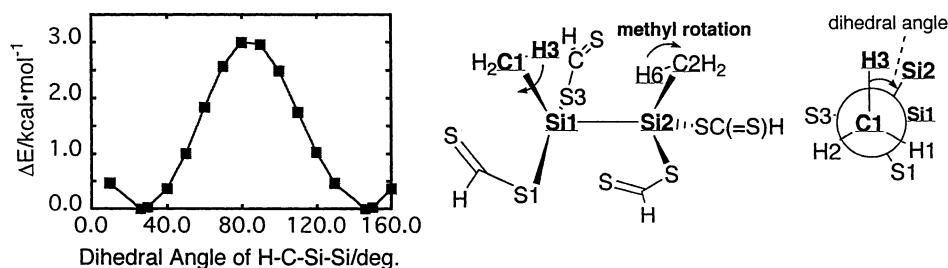
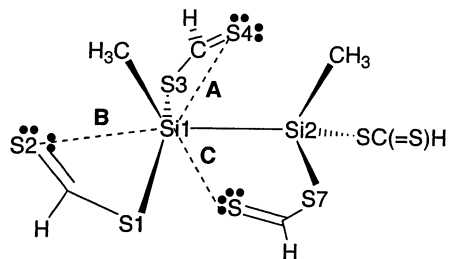


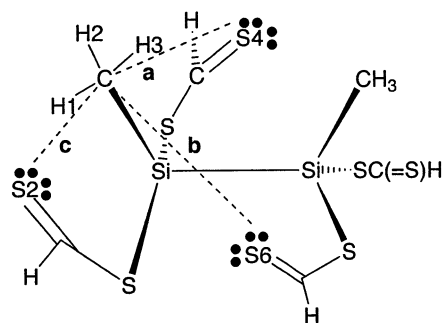
Figure 3. Energy change with methyl rotation in **2a** (RHF/LANL2DZ+p level).

Table 1. IBEs in [(HC(=S)₂MeSi)₂ **2a** for multiple hyper-coordinations (RHF/LANL2DZ//RHF/LANL2DZ+p)



	IBE/a.u.		IBE/a.u.	ΣIBE/a.u.
A: $n_S \leftrightarrow \sigma_{Si-S}$	0.0077	$n_S \rightarrow \sigma_{Si-S}^*$	-0.0821	-0.0744
B:	-0.0006	$n_S \rightarrow \sigma_{Si-Si}^*$	-0.0366	-0.0372
$n_S \leftrightarrow \sigma_{Si-Si}$				
C: $n_S \leftrightarrow \sigma_{Si-S}$	0.0072	$n_S \rightarrow \sigma_{Si-S}^*$	-0.0289	-0.0217

Table 2. IBEs in [(HC(=S)₂MeSi)₂ **2a** for hypercoordination to saturated carbon atoms (RHF/LANL2DZ//RHF/LANL2DZ+p)



	IBE/a.u.		IBE/a.u.	ΣIBE/a.u.
a: $n_{S4} \leftrightarrow \sigma_{C1-H1}$	0.0288	$n_{S4} \rightarrow \sigma_{C1-H1}^*$	-0.0372	-0.0084
b: $n_{S6} \leftrightarrow \sigma_{C1-H2}$	0.0111	$n_{S6} \rightarrow \sigma_{C1-H2}^*$	-0.0311	-0.0200
c: $n_{S2} \leftrightarrow \sigma_{C1-H3}$	0.0323	$n_{S2} \rightarrow \sigma_{C1-H3}^*$	-0.0458	-0.0135

The nearly eclipsed conformation of the C–H bond of the methyl group and the Si–Si bond was also confirmed by an X-ray crystallographic analysis of **1**.^{11,12} The dihedral angles of H–C–Si–Si are comparable to the theoretical values. Thus, these theoretical results were consistent with the X-ray analysis of **1** in the crystalline state.

Acknowledgements

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 10. We optimized the geometry of an oxygen analog $[(\text{HCO}_2)_2\text{MeSi}]_2$ **4** (Fig. 4). The distances from the center silicon atom to three oxygens are 2.900, 3.035 and 3.321 Å. These are shorter than the sum of the van der Waals radii of silicon and oxygen (3.62 Å).⁵ These results suggested hypercoordination between the lone pairs on the carbonyl oxygen atoms and Si–O bonds. However, a

C–H bond of the methyl group is anti to the Si–Si bond, indicating no appreciable hypercoordination between the lone pairs of the carbonyl oxygen atoms and the methyl carbon atoms.

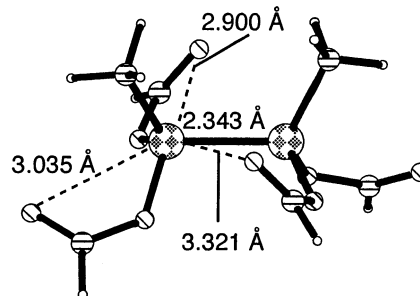


Figure 4. Optimized structure of a local minimum at the RHF/6-31G* level of **4**.

11. In Ref. 4, the hydrogen atoms of the methyl groups on silicon atoms were automatically assigned to have a staggered conformation with the Si–Si bond. We re-examined the location of these hydrogen atoms to confirm the results of the theoretical calculations. The peaks, which were assigned as hydrogen atoms, were found by Fourier methods. The C–H bonds and a Si–Si bond were located on the eclipsed conformation. See the Supporting Information for the results of an X-ray analysis of **1**.
12. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 184377.