DIMETHYLDISILYNE: A FLEETINGLY OBSERVED SPECIES INCORPORATING A TRIPLE BOND?

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We have investigated the singlet potential energy surface of $Si_2(CH_3)_2$ using ab initio self-consistent-field (SCF) methods and configuration interaction for energy comparisons. At the SCF level we find the global minimum to be silylidene, while the twist structure is also a minimum. Linear, dibridged and trans structures are found to be transition states and lie higher in energy. Our results indicate, however, that higher levels of theory are necessary for a quantitative description of the energy hypersurface. Specifically, the trans structure is stabilized greatly when the effects of electron correlation are included. The trans structure, incorporating an Si–Si bond order of roughly 2.5, is the most logical candidate for the species observed in the laboratory by West and co-workers.

1. Introduction

Although silicon lies just below carbon in the periodic table, its chemistry is surprisingly dissimilar. Much of the chemistry of carbon derives from its ability to readily form multiply bonded (and conjugated) compounds. On the other hand, it was not until 1981 that a stable Si–Si double bond was isolated [1]. Doubly bonded silicon is now well established as Si=C, Si=O, Si=N as well as Si=Si, and has been investigated extensively both experimentally [2–7] and theoretically [7–13]. Such compounds are all relatively unstable; many have only been isolated as reactive intermediates. Bulky substituent groups are necessary to stabilize the double bond by sterically preventing dimerization or other reactions. Triply bonded silicon has been more elusive, although recently Sekiguchi, Zigler and West [14] proposed dimethyldisilyne, $Si_2(CH_3)_2$, as a likely intermediate in a complex thermolysis reaction.

While no silicon–silicon triple bond has been isolated experimentally, disilyne, Si_2H_2, has a significant history of theoretical investigations [15–20]. Although acetylene (the carbon analog of disilyne) is known only in its linear form (for closed-shell electron configurations), linear Si_2H_2 is very high in energy compared to its other conformations. In fact, the most reliable theoretical studies find an unusual dibridged structure to be the global minimum on the singlet potential energy surface.

We have investigated dimethyldisilyne because of the recent experimental evidence by West and co-workers [14] for its existence as a reactive intermediate. Silicon multiple bonds are a relatively rare commodity, and theoretical studies can provide insight into the nature of these compounds. Specifically, we were interested in determining the effect of substituting the larger methyl group for hydrogens on the stability of the dibridged conformation of disilyne. We have studied at the Hartree–Fock level of theory five different conformations of $Si_2(CH_3)_2$ on the closed-shell singlet potential energy surface. Higher levels of theory are clearly required to precisely position the relative energies of the different $Si_2(CH_3)_2$ structures.

2. Theoretical approach

Optimized geometric structures for valence isomers **1–5** (see fig. 1) were obtained using analytic SCF gradient techniques [21,22] in conjunction with

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two different basis sets: (1) a standard Huzinaga–Dunning–Hay [23–25] double-zeta basis set of contracted Gaussians plus a set of d-type functions on the silicon atoms (DZ+P) and (2) basis set (1) augmented by a set of d-type functions on the carbon atoms (DZ+PP). For the DZ+P basis set, the contraction scheme is designated:

Si(11s7p1d/6s4p1d), C(9s5p/4s2p), H(4s/2s).

In this basis set there are 80 contracted Gaussians with polarization function orbital exponents $\alpha_d(\mathrm{Si})=0.50$. For the DZ+PP basis set there are 92 contracted Gaussians with polarization function orbital exponents $\alpha_d(\mathrm{Si})=0.50$, $\alpha_d(\mathrm{C})=0.75$. The DZ+PP contraction scheme is:

Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d),
H(4s/2s).

The stationary points were characterized as minima or transition states by determining the quadratic force constants and harmonic vibrational frequencies using analytic second derivative methods [26].

To check the adequacy of the one-particle basis set, the SCF wavefunction and energy were determined for each conformer at the DZ+PP optimized geometry using an extended basis set (EXT). This consisted of Dunning's 5s3p contraction [24] of the same 9s5p primitive set plus a set of d functions on carbon with the same orbital exponents as before and a standard double-zeta basis plus a set of p functions on hydrogen ($\alpha_d=0.75$). For the silicon atoms we use McLean and Chandler's [27] contraction of Huzinaga's 12s9p primitive Gaussians augmented with two sets of d-functions with orbital exponents of $\alpha_d=1.0$, 0.25:

Si(12s9p2d/6s5p2d).

For final energetic comparisons, electron correlation effects have been included via the method of configuration interaction [28] for each conformer using both of the basis sets DZ+P and DZ+PP. Only the valence electrons have been correlated explicitly; the core-like orbitals (Si 1s, 2s, 2p; C 1s) and their virtual orbital counterparts were not included in the CI. Otherwise, all single and double excitations from the SCF reference configuration have been included (CISD).

3. Results and discussion

The SCF optimized geometries for the five conformations of $Si_2(CH_3)_2$ are shown in fig. 1. Values are given for both the DZ+PP and the DZ+P (in parentheses) basis sets. The results are repeated in table 1 for comparison with the DZ+P Si_2H_2 results of Clabo and Schaefer [20]. We began our investigation by optimizing the linear structure (**1**) in C_{2h} symmetry. The ground state is $^1A_{1g}$, with an electron configuration (expressed in C_{2h} orbitals):

$$[\mathrm{core}]\,6a_g^2\,6b_u^2\,7a_g^2\,2a_u^2\,7b_u^2\,8a_g^2\,2b_g^2\,8b_u^2\,9a_g^2\,3a_u^2\,9b_u^2.$$

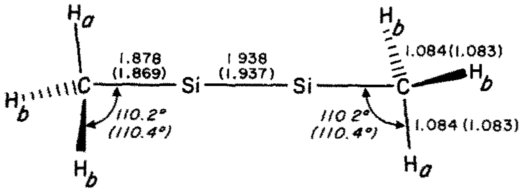
We find the Si–Si triple bond distance to be 1.938 Å (1.937 Å) for the DZ+PP (DZ+P) basis. Thus, comparing with Si_2H_2, we see that, to within 0.001 Å, this bond length is independent of substituent. From the second derivative analysis, the Si–Si stretching frequency occurs at 503 cm^{-1} (510 cm^{-1}). Molecular structures can be classified as minima, transition states or higher-order saddle points by the number of imaginary harmonic vibrational frequencies; a minimum on the potential energy surface having no imaginary frequencies, and a transition state having one. For the linear structure of $Si_2(CH_3)_2$, we find one doubly degenerate imaginary frequency at 229i cm^{-1} (231i cm^{-1}). Analysis of the corresponding eigenvectors shows that this normal mode leads to the trans structure (**2**).

We then optimized the trans conformer in its full C_{2h} symmetry. We obtained a ^1A_g ground state with electron configuration:

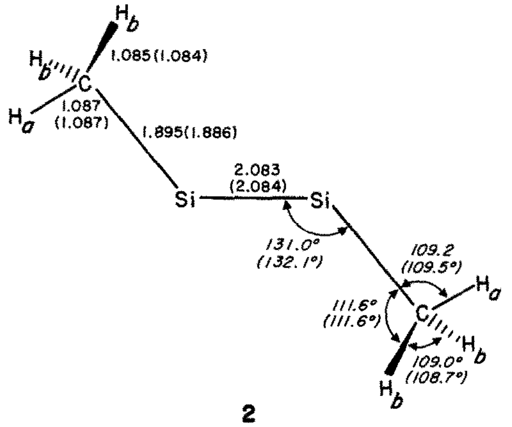
$$[\mathrm{core}]\,6a_g^2\,6b_u^2\,7a_g^2\,7b_u^2\,2a_u^2\,2b_g^2\,8a_g^2\,8b_u^2\,9a_g^2\,9b_u^2\,3a_u^2.$$

The Si–Si bond length of 2.083 Å (2.084 Å) is 0.0007 Å longer than for Si_2H_2. This is slightly shorter than expected for a typical Si–Si double bond. Experimentally the double bond distance has been reported to be 2.16 Å [3]. The C–Si–Si angle of 131.0° (132.1°) is slightly larger than the H–Si–Si angle (127.3°) in Si_2H_2. The Si–Si stretching frequency is 472 cm^{-1} (473 cm^{-1}), and the one imaginary vibrational frequency at 29i cm^{-1} (32i cm^{-1}) leads toward the twist isomer (**3**).

The lowest singlet state of the twist structure (**3**) is a ^1A state of C_2 symmetry with electron configuration:



1



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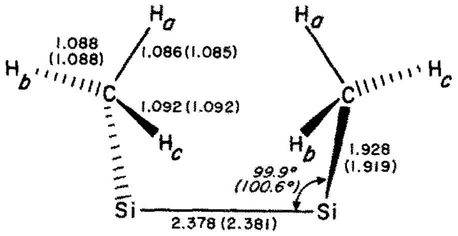
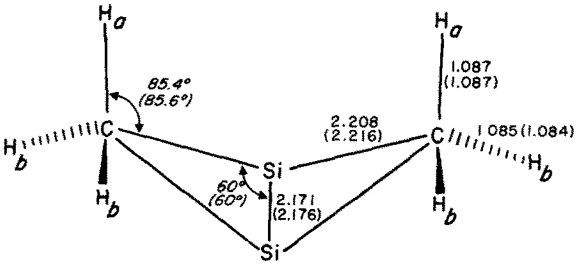


3 $\phi_{C-Si-Si-C}$ = 97.2 (96.8)



4 $\phi_{C-Si-Si-C}$ = 97.2 (105.0)

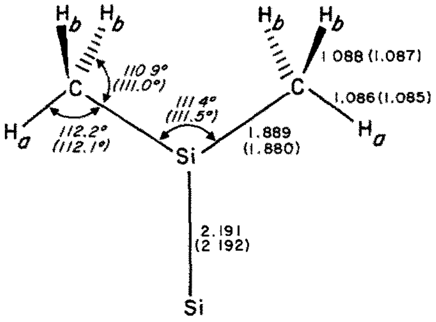


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Fig. 1. The five conformations of $Si_2(CH_3)_2$. Optimized geometries are with the DZ+PP and DZ+P (in parentheses) bases. Bond lengths are in Å and angles in deg.

$$[\text{core}]7a^2 7b^2 8a^2 8b^2 9a^2 9b^2 10a^2 10b^2 11a^2 11b^2 12a^2.$$

The Si–Si bond length of 2.378 Å (2.381 Å) is consistent with a single bond and 0.037 Å shorter than for twisted Si_2H_2. However, both the C–Si–Si angle of 99.9° (100.6°) and the dihedral C–Si–Si–C angle of 97.2° (96.8°) are significantly larger than for Si_2H_2, suggesting the emergence of steric effects from the larger methyl group. The Si–Si stretch occurs at 382 cm^{-1} (380 cm^{-1}). The absence of any imaginary vibrational frequencies indicates that the twist conformer of $Si_2(CH_3)_2$ is a minimum on the singlet potential energy surface, at least at the single-configuration self-consistent-field (SCF) level of theory.

Taking our cue from Si_2H_2, we next investigated the dibridged conformation (**4**). Within the confines of C_{2v} symmetry, we located a stationary point with electron configuration:

$$[\text{core}]6a_1^2 3b_2^2 7a_1^2 5b_1^2 8a_1^2 2a_2^2 4b_2^2 5b_2^2 6b_1^2 9a_1^2 10a_1^2.$$

This rather unusual structure was determined to be the global minimum for the analogous Si_2H_2 system in several theoretical studies [17,19,20]. For $Si_2(CH_3)_2$, however, the dibridged structure is a structure of Hessian index two, with two imaginary vibrational frequencies of 155i cm^{-1} (159i cm^{-1})

Table 1
Optimized geometries for Si$_2$R$_2$ with the DZ+P and DZ+PP basis. Bond lengths are in Å and angles in deg. The Si$_2$H$_2$ predictions are from ref. [20]

		R=H DZ+P	R=CH$_3$	
			DZ+P	DZ+PP
linear (**1**)	r(Si–Si)	1.937	1.937	1.938
	r(Si–R)	1.445	1.869	1.878
	r(C–H$_a$)	–	1.083	1.084
	r(C–H$_b$)	–	1.083	1.084
	θ(H$_a$–C–Si)	–	110.4	110.2
	θ(H$_b$–C–Si)	–	110.4	110.2
dibridged (**4**)	r(Si–Si)	2.183	2.176	2.171
	r(Si–R)	1.664	2.216	2.208
	θ(R–Si–Si)	49.0	60.0	60.0
	ϕ(R–Si–Si–R)	102.7	105.0	97.2
	r(C–H$_a$)	–	1.087	1.087
	r(C–H$_b$)	–	1.084	1.085
	θ(H$_a$–C–H$_b$)	–	107.7	107.7
	θ(H$_b$–C–H$_b$)	–	104.3	104.0
	θ(H$_a$–C–Si)	–	85.6	85.4
trans (**2**)	r(Si–Si)	2.077	2.084	2.083
	r(Si–R)	1.469	1.886	1.895
	θ(R–Si–Si)	127.3	132.1	131.0
	r(C–H$_a$)	–	1.087	1.087
	r(C–H$_b$)	–	1.084	1.085
	θ(H$_a$–C–Si)	–	109.5	109.2
	θ(H$_b$–C–Si)	–	111.5	111.6
	θ(H$_b$–C–H$_b$)	–	108.7	109.0
twist (**3**)	r(Si–Si)	2.344	2.381	2.378
	r(Si–R)	1.509	1.919	1.928
	θ(R–Si–Si)	88.3	100.6	99.9
	ϕ(R–Si–Si–R)	88.3	96.8	97.2
	r(C–H$_a$)	–	1.085	1.086
	r(C–H$_b$)	–	1.088	1.088
	r(C–H$_c$)	–	1.092	1.092
	θ(H$_a$–C–H$_b$)	–	108.1	108.1
	θ(H$_b$–C–H$_c$)	–	106.4	106.3
	θ(H$_a$–C–Si)	–	111.1	111.3
	θ(H$_c$–C–H$_a$)	–	107.2	106.9
	θ(H$_b$–C–Si)	–	114.4	115.4
	θ(H$_c$–C–Si)	–	109.4	108.3
silylidene (**5**)	r(Si–Si)	–	2.192	2.191
	r(Si–R)	–	1.880	1.889
	θ(R–Si–R)	–	111.5	111.4
	r(C–H$_a$)	–	1.085	1.086
	r(C–H$_b$)	–	1.087	1.088
	θ(H$_a$–C–H$_b$)	–	107.6	107.6
	θ(H$_b$–C–H$_b$)	–	107.5	107.5
	θ(H$_a$–C–Si)	–	112.1	112.5
	θ(H$_b$–C–Si)	–	111.0	110.9

and 280i cm^{-1} (285i cm^{-1}). The former normal mode corresponds to motion of both methyl groups toward one of the silicons, leading to the silylidene structure (5). The latter corresponds to motion of the methyl groups toward separate silicon atoms, or toward the twist structure (3), which we have already discussed. The Si–Si stretching frequency is 643 cm^{-1} (622 cm^{-1}). The Si–Si distance of 2.171 Å (2.175 Å) is indicative of a double bond. The C–Si–Si–C dihedral angle of 97.2° (105.0°) is only 2° different from the H–Si–Si–H angle in Si_2H_2 at equivalent levels of theory (DZ+P). Thus the substitution of CH_3 for H apparently does not cause crowding in this structure. While the R–Si–Si angle is much larger for $Si_2(CH_3)_2$ than for Si_2H_2, this results from the greater length of the C–Si bond and the constraints of the C_{2v} geometry – the carbon must form an equilateral triangle with the two silicons.

Following the unexplored imaginary frequency of the dibridged isomer, we arrive at dimethyl silylidene (5), and discover that it is a minimum. This structure has C_{2v} symmetry, and the ground electronic configuration is:

$$[\text{core}]8a_1^2 4b_2^2 9a_1^2 10a_1^2 3b_1^2 5b_2^2 1a_2^2 11a_1^2 6b_2^2 12a_1^2 4b_1^2.$$

The Si–Si double bond has a length of 2.191 Å (2.192 Å) and a stretching frequency of 506 cm^{-1} (509 cm^{-1}). The C–Si–C angle of 111.4° (111.5°) is smaller than expected for sp^2 hybridization (120°).

Table 2 compares the SCF and CISD relative and total energies for the three basis sets employed. For the Davidson-corrected CISD (CISD+Q) approach, the effects of unlinked quadruple excitations have been included in an approximate manner via Davidson's formula [29]. The lowest energy structure is silylidene, independent of basis size and level of theory. At the Hartree–Fock level, the energy ordering (increasing) is: silylidene, twist, trans, dibridged, linear. There is a slight exception for the DZ+P basis, where the dibridged conformer is slightly higher in energy than the linear. The CISD results are different, with energy ordering: silylidene, trans, twist, dibridged, linear. Inclusion of electron correlation stabilizes the trans isomer, so that it lies lower than the twist structure in energy. This strongly suggests that the trans structure may in fact be a minimum at the correlated level of theory. The latter conclusion is consistent with the high level theoretical findings of Somasundram, Amos and Handy [13] for the related Si_2H_4 system.

The large correlation energy of the trans structure arises because of the importance of several electronic

Table 2
Total energies in hartree and relative energies in kcal/mole for the DZ+P, DZ+PP, and EXT basis sets

		DZ+P		DZ+PP		EXT	
		kcal/mole	hartree	kcal/mole	hartree	kcal/mole	hartree
linear	SCF	34.7	−656.905 778	34.1	−656.930 840	35.2	−656.984 290
	CISD	30.7	−657.232 041	31.0	−657.328 788	–	–
	CISD+Q	30.0	−657.278 869	30.3	−657.387 370	–	–
dibridged	SCF	35.2	−656.904 971	33.5	−656.931 884	32.0	−656.989 311
	CISD	26.7	−657.238 464	24.9	−657.338 449	–	–
	CISD+Q	24.7	−657.287 280	22.8	−657.399 349	–	–
trans	SCF	20.3	−656.928 606	20.2	−656.953 187	21.9	−657.005 016
	CISD	12.2	−657.261 549	12.9	−657.357 621	–	–
	CISD+Q	8.8	−657.312 546	9.7	−657.420 177	–	–
twist	SCF	14.8	−656.937 409	14.5	−656.962 213	15.2	−657.016 123
	CISD	17.3	−657.253 410	16.7	−657.351 516	–	–
	CISD+Q	17.7	−657.298 338	17.2	−657.408 190	–	–
silylidene	SCF	0.0	−656.961 026	0.0	−656.985 309	0.0	−657.040 318
	CISD	0.0	−657.281 000	0.0	−657.378 167	–	–
	CISD+Q	0.0	−657.326 612	0.0	−657.435 596	–	–

Table 3
CI coefficients greater than 0.05 and corresponding valence configurations

Conformer	Coefficient		Configuration
	DZ+P	DZ+PP	
silylidene	0.926	0.924	ground state
	−0.088	−0.079	$4b_2^2 \rightarrow 5b_2^2$
linear	0.925	0.923	ground state
	−0.065	−0.059	$3b_1^2 \rightarrow 3a_2^2$
	0.065	0.059	$9b_2^2 \rightarrow 10a_1^2$
	0.057	−0.052	$3b_1 9b_2 \rightarrow 3a_2 10a_1$
dibridged	0.924	0.922	ground state
twist	0.926	0.924	ground state
trans	0.920	0.919	ground state
	−0.097	−0.086	$9b_2^2 \rightarrow 10a_1^2$
	0.076	0.068	$3b_1^2 \rightarrow 3a_2^2$
	0.075	0.067	$3b_1 9b_2 \rightarrow 3a_2 10a_1$
	−0.051	−0.050	$3b_1 9b_2 \rightarrow 3a_2 10a_1$

structures. In table 3 we report the CI coefficients above 0.05 (at least 0.25% of the wavefunction) and the corresponding electronic structures. The linear and silylidene isomers also appear to have more than a single important configuration. This suggests, that a quantitative prediction of the energy ordering of the conformers of $Si_2(CH_3)_2$ will require a multi-reference CI treatment including at least the valence π electrons.

4. Conclusions

We conclude that $Si_2(CH_3)_2$ is very different from its carbon analog, $C_2(CH_3)_2$, which exists as linear dimethyl acetylene, and from the parent silicon compound Si_2H_2. For $Si_2(CH_3)_2$ the linear form is the least stable of the structures investigated, while the preferred structure is the silylidene. This result comes as no great surprise since second-row atoms are traditionally reluctant to engage in π-bonding [30]. Also, the stability of the divalent state increases going down group IV (i.e. carbon to silicon) [31–33], suggestive of a stable silylidene structure. Other supportive evidence is the facile 1,2-hydrogen shift in doubly bonded silicon compounds; this rearrangement is observed more readily for silicon than for carbon [12,33]. It is known, for example, that silaethylene lies only about 5 kcal/mole below methylsilylene [33]. Thus the location of a lone pair on silicon is energetically comparable to forming a multiple bond and greatly preferable to having a lone pair on carbon. This is seen in the theoretical finding that the silylidene H_2S=Si: is a very low-lying isomer of Si_2H_2. Binkley [19] found that this lies 11.3 kcal/mol above the dibridged structure, while Lischka and Köhler [17] found the energy difference to be 5.8 kcal/mol at the Hartree–Fock level and 11.0 kcal/mol at the CEPA level.

Comparing $Si_2(CH_3)_2$ with Si_2H_2, the most noticeable change is the destabilization of the dibridged conformer. A low-lying minimum for Si_2H_2, this structure is a high-lying transition state for the methyl-substituted isomer. This energetic effect is partially due to steric interference of the bridging methyl groups, although this is not apparent geometrically where we find similar dihedral angles for the two molecules. Also, the spherical orbitals of hydrogen overlap more effectively with the silicons from a bridging position than do the 2p orbitals of carbon.

Another interesting effect of substituting methyl groups for hydrogen in Si_2H_2 is the reversal in relative ordering of the twist and trans conformers at the Hartree–Fock level. Inclusion of electron correlation, however, shifts the trans structure below the twist again.

As expected, our results indicate that the relative energies of the $Si_2(CH_3)_2$ conformers demonstrate strong basis set dependence, with the inclusion of polarization functions on both silicon and carbon being crucial. In addition, the inclusion of electron correlation via CI changes significantly both the relative energies and the energetic ordering of the conformers. Further work on this molecule should thus involve multi-reference CI wavefunctions constructed from large basis sets.

The silylidene minimum structure of $Si_2(CH_3)_2$ clearly demonstrates the different behavior of silicon-based compounds compared to their carbon analogs. In addition, the behavior of silicon also exhibits a large dependence on substituents. For example, the behavior of $Si_2(CH_3)_2$ cannot be simply predicted from that of Si_2H_2.

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