

## An *Ab initio* Comparative Study of Bicyclo[1.1.0]tetrasilane and Bicyclo[2.2.0]hexasilane

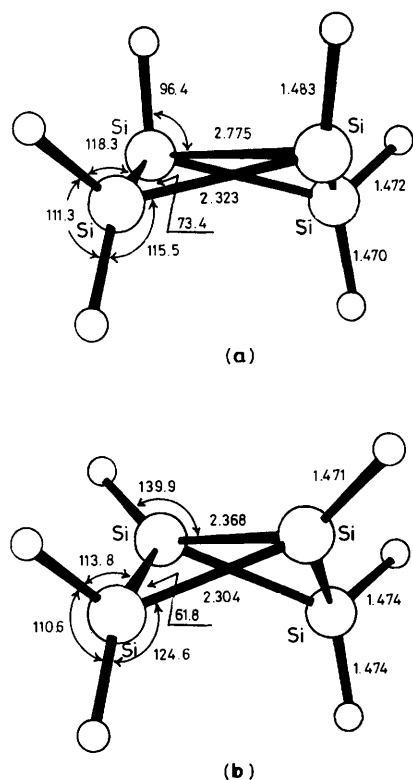
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*Ab initio* calculations show that bicyclo[2.2.0]hexasilane has a normal central bond, unlike the more strained bicyclo[1.1.0]tetrasilane, and is much less strained than its carbon analogue bicyclo[2.2.0]hexane.

Interest in the silicon analogues of polycyclic hydrocarbons has increased substantially in recent years. The first synthetic example was made in 1985 for a bicyclo[1.1.0]tetrasilane derivative and its *X*-ray structure has been determined by Masamune *et al.*<sup>1,2</sup> In view of the growing interest in the properties and preparation of bicyclo[*m.n.0*]polysilane, we

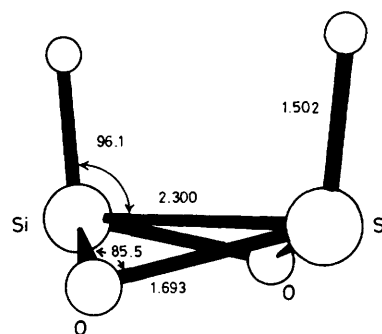
report here the *ab initio* comparison of bicyclo[1.1.0]tetrasilane (**1**) and bicyclo[2.2.0]hexasilane (**2**). Geometries were fully optimized at the Hartree–Fock (HF) level with the split-valence 3-21G<sup>3</sup> and polarized 6-31G\*<sup>4</sup> basis sets, and identified as equilibrium or transition structures by diagonalizing the Hessian matrices at the HF/3-21G level.



**Figure 1.** The HF/6-31G\* optimized geometries of two isomers (a) and (b) of (1) with  $C_{2v}$  symmetry in Å and degrees. The interflap angles between the three-membered rings are 142.0° (a) and 122.8° (b). The total energies are -1159.08163 (a) and -1159.07739 (b) Hartrees.

For (1), Schleyer *et al.* have predicted that there are two distinctly different energy minima (a) and (b) (Figure 1).<sup>5</sup> A key geometrical difference between these two minima is in the central bridge Si-Si distances [ca. 2.78 Å for (a) vs. 2.37 Å for (b)]. The bond-stretch isomer (a) was also calculated at the HF/4-31G level by Dabisch and Schoeller,<sup>6</sup> while only the shorter bond length isomer (b) has recently been located at the HF/6-31G\* level by Collins *et al.*<sup>7</sup> This discrepancy was ascribed to the difference in the basis sets used,<sup>7</sup> since (b) corresponds more closely to Masamune's experimental structure.<sup>†</sup> As Figure 1 shows, however, we have located a minimum of structure (a) even with the 6-31G\* basis set, this being 2.7 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ) more stable than that located by Collins *et al.*<sup>7</sup> Inclusion of electron correlation *via* full fourth-order Møller-Plesset perturbation theory<sup>8</sup> (MP4SDTQ/6-31G\*/6-31G\*) makes the bond stretch isomer more stable by 8.2(MP2), 8.0(MP3), and 8.9(MP4) kcal mol<sup>-1</sup>. The MC-SCF pseudopotential calculations with an unpolarized basis set gave an even greater energy difference of 17 kcal mol<sup>-1</sup> favouring (a) over (b).<sup>5</sup> Thus, structure (a) will be considered for (1) in the following analysis.

In a recent study,<sup>9</sup> we have shown that the long central Si-Si bond (2.719 Å) in pentasil[1.1.1]propellane (having three three-membered rings fused to its central bond) is considerably shortened by oxygen-substitution. Thus, the peripheral SiH<sub>2</sub> groups in (1) were substituted by O atoms. As Figure 2 shows, the dioxasubstitution leads to a single structure of type (a) and results in shrinking the central Si-Si bond to 2.300 Å.



**Figure 2.** 2,4-dioxabicyclo[1.1.0]tetrasilane located at the HF/6-31G\* level. The interflap angle and total energy are 140.6° and -728.67648 Hartrees, respectively.

**Table 1.** Comparison of the vibrational frequencies (cm<sup>-1</sup>) of (2) and (4) calculated at the HF/3-21G level.<sup>a</sup>

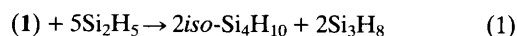
$a_1$ sym.	$a_2$ sym.	$b_1$ sym.	$b_2$ sym.
118 (413)	37 (41)	304 (804)	102 (359)
313 (778)	221 (713)	387 (949)	306 (970)
370 (864)	364 (962)	429(1090)	352 (800)
389 (954)	423(1050)	551(1149)	468(1222)
399 (995)	600(1409)	696(1436)	587(1311)
621(1248)	683(1340)	750(1357)	732(1376)
668(1329)	748(1417)	962(1645)	745(1432)
773(1409)	957(1626)	2263(3241)	961(1639)
973(1661)	2257(3231)	2277(3293)	2257(3232)
2263(3243)	2270(3272)		2269(3294)
2279(3311)			2275(3274)
2283(3295)			

<sup>a</sup> Values in parentheses are for the corresponding frequencies of the carbon compound.

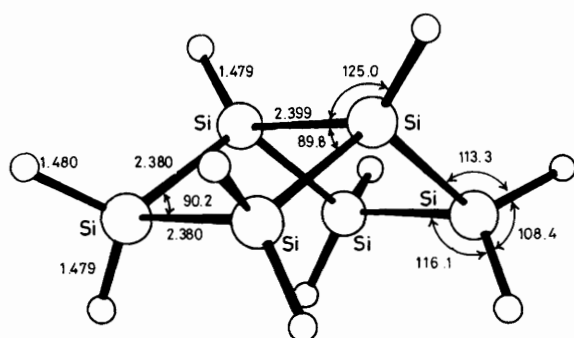
However, it was found that the dioxasubstituted (1) is not a minimum but a transition structure (leading to Si<sub>2</sub>O<sub>2</sub> + 2H). In another attempt, two H atoms on the bridgehead positions in (1) were replaced by two F atoms. However, this resulted in destroying completely the central Si-Si bond. These results suggest that the electronic effect of substituents is unlikely to shorten significantly the central Si-Si bond of (1).

For (2), we have located a single minimum, as characterized by all real vibrational frequencies in Table 1. As Figure 3 shows, the central (2.399 Å) and peripheral (2.380 Å) Si-Si bond lengths in (2) are rather normal compared with those in the four-membered rings of cyclotetrasilane (2.373 Å),<sup>10</sup> octasilacubane (2.396 Å),<sup>10</sup> and octasila[2.2.2]propellane (2.381–2.393 Å).<sup>9</sup> In order to examine the possibility of a bond-stretch isomer, a series of HF/6-31G\* single-point calculations were carried out with several fixed central Si-Si distances, all other geometrical parameters being fully optimized at the HF/3-21G level. As a result, it was found that the energy increases significantly as the central bridge bond length increases: 0.0(2.464 Å), 6.9(2.7 Å), 21.0(3.0 Å), 36.0(3.3 Å), and 50.1(3.6 Å) kcal mol<sup>-1</sup>. This indicates that there is no second minimum corresponding to a bond-stretch isomer as in the case of (1).

The strain energies of (1) and (2) were calculated from the homodesmotic reactions<sup>11</sup> by using the HF/6-31G\* total energies, equations (1) and (2). For comparison, the strain of



<sup>†</sup> It is suggested<sup>5</sup> that a short central Si-Si bond (2.373 Å) in Masamune's experimental structure<sup>2</sup> is due to the special requirements of the bulky bridgehead substituents.



**Figure 3.** The HF/6-31G\* optimized geometries of (2) with  $C_{2v}$  symmetry in Å and degrees. The interflap angle and total energy are  $112.6^\circ$  and  $-1739.29704$  Hartrees, respectively.

their carbon counterparts, bicyclo[1.1.0]butane (3) and bicyclo[2.2.0]hexane (4), were also calculated in the same way. The calculated strain energies were  $65.2(1)$ ,  $32.2(2)$ ,  $68.9(3)$ , and  $53.8(4)$  kcal mol $^{-1}$ , the last two values for the carbon compounds agreeing well with the experimental evaluation of 63.9 and 51.8 kcal mol $^{-1}$ ,<sup>12</sup> respectively. An interesting finding is that the strain energy in (1) is essentially comparable to that in its carbon counterpart (3). This trend is also found in the polyhedral silicon and carbon compounds consisting only of three-membered rings; tetrasilatetrahdrane (140.9 kcal mol $^{-1}$ ) vs. tetrahdrane (141.4 kcal mol $^{-1}$ ).<sup>10</sup> Upon conversion of the three-membered rings in (1) to the four-membered rings in (2), the strain energy decreases substantially. This relief of strain (33 kcal mol $^{-1}$ ) is more than twice that (15.1 kcal mol $^{-1}$ ) in the carbon compounds, reflecting the fact that four-membered rings are less strained in silicon compounds.<sup>9,10</sup> The strain energy of (2) consequently becomes ca. 22 kcal mol $^{-1}$  less than that of (4).

In general, polycyclic silicon compounds with four-membered rings are considerably less strained than their carbon analogues, and therefore have a normal structure despite relatively weak Si-Si bonds.<sup>13</sup> The derivatives of (2) also form interesting synthetic targets.

Calculations were carried out at the Computer Center of the Institute of Molecular Science using the Gaussian 82 program.<sup>14</sup> This work was supported in part by the Ministry of Education, Science, and Culture in Japan (Grant-in-Aid for Special Project Research).

*Note added in proof.* The first bicyclo[2.2.0]hexasilane system, decaisopropylbicyclo[2.2.0]hexasilane, has very recently been synthesized (H. Matsumoto, H. Miyanoto, N. Kojima, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1987, 1316).

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