Structure and Bonding in B₁₀X₂H₁₀ (X = C and Si). The Kinky Surface of 1,2-Dehydro-*o*-disilaborane

Eluvathingal D. Jemmis* and Boggavarapu Kiran

School of Chemistry, University of Hyderabad
Hyderabad 500046, India

The chemistry of *o*-carborane (**1**) has several parallels with benzene.[1–3] Jones and co-workers[4] have brought out yet another amazing parallel between these two prototypes: the 1,2-dehydro-*o*-carborane (**2**) is shown to be comparable in reactivity to 1,2-dehydrobenzene (benzyne) (**3**). Derivatives of disila-analogs should provide equally interesting chemistry. Seyferth and co-workers[5] have synthesized a dimethyl derivative of **4**. Despite

1   **2**   **3**   **4**

Distances at B3LYP/6-31G*
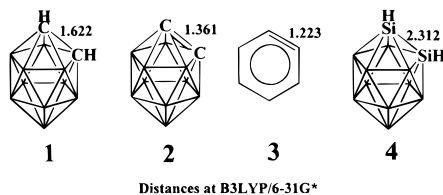
the structural similarity between **1** and **4**, they differ substantially in their reactivity patterns. Nucleophilic bases attack the dimethyl derivative of **4** resulting in the loss of an MeSi vertex; whereas, in **1** the reaction is centered on a boron adjacent to the carbon.[6] Will the behavior of B₁₀Si₂H₁₀ follow that of the carbon analog? The structure of Si₂H₄ contrast dramatically with that of ethylene.[7,8] Constraints of an icosahedral skeleton make any guess on the structure of the B₁₀Si₂H₁₀ even more hazardous. This paper compares the C–C double bonds in **2** and **3** and unravels an unexpected kinky structure for B₁₀Si₂H₁₀.

The structures **1–6** and **11** were optimized at the HF/6-31G* and B3LYP/6-31G* levels of theory.[9,10] Total energies and important parameters are given in Table 1. Unless otherwise stated, B3LYP energies and bond parameters are used in the discussion. The structure of *o*-carborane has been studied by several theoretical methods.[11] The structure is calculated to be

5   **6**   **11**

Distances at B3LYP/6-31G* except for 11 (HF/6-31G*)

a minimum at the B3LYP/6-31G* level with a C–C distance, 1.622 Å, comparable to the experimental value (Table 1) and to the previous theoretical studies. The Wiberg bond index[12] (WBI) of 0.74 reflects the stretched and delocalized nature of the C–C bond. For comparison, WBI for C–C bond in ethane is 1.00. The 1,2-dehydro-*o*-carborane (**2**) is also calculated to be a minimum with a C–C distance of 1.361 Å. This is much longer than the corresponding C–C distance in benzyne but no direct comparison can be made as there is no previous theoretical or experimental estimate.

The frontier orbitals of **2** and **3** are the π and the π* levels. The LUMO energies for **2**, **3**, and ethylene are −0.1438, −0.0702, and 0.0188 au, respectively. Therefore, in Diels–Alder reactions, the reactivity toward normal dienes is expected to be in the order **2** > **3** > C₂H₄, if steric considerations are not taken into account. The π bonds in **2** and **3** are destabilized in relation to ethylene by similar amounts (eqs 1 and 2). These are in tune with the observed experimental reactivities.[4b]

$$C_2H_6 + 2 \rightarrow 1 + C_2H_4 \qquad -57.4 \text{ kcal/mol} \qquad (1)$$

$$C_2H_6 + 3 \rightarrow C_6H_6 + C_2H_4 \qquad -60.1 \text{ kcal/mol} \qquad (2)$$

The calculated Si–Si distances in **4** of 2.309 Å (HF) and 2.312 Å (B3LYP) are comparable to the experimental distance of 2.308 Å (Table 1). This is shorter than the Si–Si bond distance in (CH₃)₆Si₂, 2.340 Å.[13] The dehydro structure **5** is calculated to have an Si–Si distance of 2.164 Å at the HF level and 2.229 Å at the B3LYP level of theory. In contrast to the increase in the Si≡Si distance in **5** on going to the B3LYP level, the B–B bonds which are involved heavily in the multicenter bonding of the cage are shortened at this level, (HF av B–B = 1.825 Å; B3LYP av B–B = 1.809 Å). The influence of the icosahedral skeleton in determining the relative π bond strengths is demonstrated by eqs 3 and 4.

$$H_2Si=SiH_2 + C_2H_6 \rightarrow$$
$$Si_2H_6 + H_2C=CH_2 \qquad -19.0 \text{ kcal/mol} \quad (3)$$

$$1 + 5 \rightarrow 2 + 4 \qquad 36.6 \text{ kcal/mol} \qquad (4)$$

The exothermicity of eq 3 is attributed among other factors to the strong C–C π bonds. However, the eq 4 is endothermic. A probable explanation for the reversal could be obtained from the structural details of the icosahedral skeletons. The B–B

(1) (a) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry;* Wiley: New York, 1987. (b) Muetterties, E. L. *Boron Hydride Chemistry;* Academic Press: New York, 1975. (c) Grimes, R. N. *Carboranes;* Academic Press: New York, 1970. (d) Onak, T. *Organoborane Chemistry;* Academic Press: New York, 1975. (e) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.

(2) *Gmelin Handbook of Inorganic Chemistry,* 8th ed.; Springer Verlag: Berlin, 1988; 3rd Supplement, Vol. 4.

(3) (a) Zakharkin, L. I.; Pisareva, I. V.; Bikkineev, R. K. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.) **1977**, 577. (b) Andrews, J. S.; Zyas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715. (c) Albagli, D.; Zheng, G.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 129 and references therein.
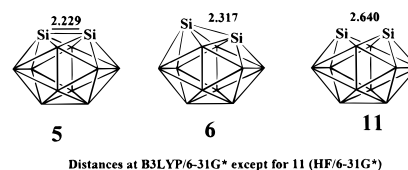
(4) (a) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4082. (b) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313. (c) Huang, Q.; Gingrich, H. L.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254. (d) Cunningham, R. J.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1994**, *33*, 4811. (e) Ho, D. M.; Cunningham, R. J.; Brewer, J.; Judson, A.; Bian, N.; Jones, M., Jr. *Inorg. Chem.,* **1995**, *34*, 5274.

(5) (a) Seyferth, D.; Buchner, K.; Rees, W. S., Jr.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 918. (b) Seyferth, D.; Buchner, K. D.; Rees, W. S., Jr.; Wesemann, L.; Davis, W. M.; Bukalov, S. S.; Leites, L. A.; Bock, H.; Solouki, B. *J. Am. Chem. Soc.* **1993**, *115*, 3586.

(6) (a) Wesemann, L.; Englert, U.; Seyferth, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2236. (b) Wesemann, L.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 527.
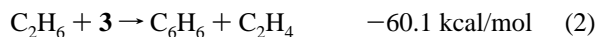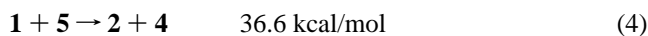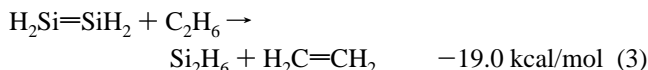
(7) (a) Tsumurya, T.; Batchellers, A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (b) West, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1201.

(8) (a) Grev, R. S.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *97*, 7990 and references therein. (b) Jocobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667 and references therein.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.1;* Gaussian Inc.: Pittsburgh, PA, 1995.

(10) (a) B3LYP is Becke's three parameter hybrid method using the LYP correlation functional. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Vosoko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(11) Martin, D.; Jaballas, J.; Arias; J.; Lee, H.; Onak, T. *J. Am. Chem. Soc.* **1996**, *118*, 4405 and references therein.

(12) (a) Reed, A. E.; Weistock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735 and references therein. (b) Reed, A. E.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 and references therein.

(13) Beagley, J. J.; Monaghan, T. G.; Hewis, J. *J. Mol. Struct.* **1971**, 401.

Table 1. Total and Relative Energies (RE) at HF/6-31G* and B3LYP/6-31G* Levels and Important Parameters of Various Isomers

	total energy (au)		RE (kcal/mol)		X−X (Å)			WBI	
	HF	B3LYP	HF	B3LYP	HF	B3LYP	exptl	HF	B3LYP
1	−329.62084(0)	−332.10450(0)			1.609	1.622	1.624	0.75	0.74
2	−328.30841(0)	−330.77019(0)			1.322	1.361		1.75	1.65
3	−229.38685(0)	−230.90995(0)			1.251	1.223		2.45	2.36
4	−831.69385(0)	−834.87366(0)			2.309	2.312	2.308	0.56	0.49
5	−830.39606(1)	−833.57328(1)	13.7	5.2	2.164	2.229		1.58	0.98
6	−830.41788(0)	−833.58160(0)	0.0	0.0	2.300	2.317		0.68	0.51
11	−830.38162(3)	collapsed to **5**	22.8		2.640			0.02	

distance in $B_{12}H_{12}^{2-}$ is 1.800 Å. To accommodate this skeletal distance, the C−C bond in **1** is stretched to 1.624 Å. The strain goes up further in **2**, because the C−C double bond is energetically more expensive to stretch. The calculated distance of 1.361 Å in **2** is only marginally longer than that in ethylene. The structure is distorted considerable from an ideal skeleton. Another source of strain is the pyramidalization of the carbon in **2**. A contraction, instead of elongation, is in order in **4**; the Si−Si distance decreases to 2.312 Å. This is still far from the standard icosahedral value of 1.800 Å in $B_{12}H_{12}^{2-}$. Further reduction of strain is achieved in the silicon system by introducing the double bond (**5**). In addition, the pyramidalization at Si is less-demanding energetically. Thus, the combination of **1** and **5** is better compared to **2** and **4**. Despite this **5** is calculated to be a transition state. Following the imaginary frequency led to an unusual structure **6** with C_s symmetry.

The surface of **6** is kinky. One Si atom has gone out of the icosahedral surface (Si$_{out}$) and the other has gone slightly in (Si$_{in}$). The average Si−B bond distance of 2.121 Å in **5** has gone to 2.360 Å for the Si$_{out}$ and 2.043 Å for the Si$_{in}$. The Si−Si distances and WBI values in **4** (2.309 Å, 0.57) and **6** (2.300 Å, 0.67) are comparable. However, the Si−Si bond in **6** is very different from that in **4**. The results indicate that a good approximation to bonding can be obtained starting with the interaction of two sp^2 hybrid Si groups. In a symmetrical arrangement as in **5**, there is a σ orbital and a π orbital (**7**). In

7　　**8**

9　　**10**
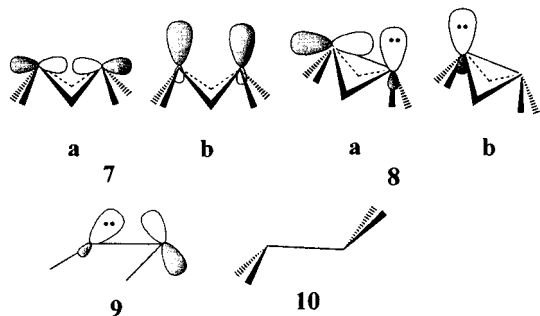
6, one Si goes up and the other goes down, resulting in two

different MOs (**8**). The σ MO (**8a**) arises from the interaction of the p orbital on Si$_{out}$ with the sp^n hybrid on Si$_{in}$. A lone pair formed on Si$_{out}$ is the HOMO (**8b**). There are a few examples in literature where the p orbital of one Si is accepting electrons from the hybrid orbital of the adjacent Si. Monobridged Si_2H_2 (**9**) presents the closest comparison.[14] Even though the environment around Si is very different in **6** and **9**, the Si_2H_2 structure presents such an interaction.[14] The Si_2 unit in **6** can also be compared to that in Si_2H_4 (**10**). The trans structure **10** is calculated to be more favorable than the cis structure; the latter is not even a stationary point.[8b] However, the constraints of the B_{10} template forces a cis arrangement with the unusual bonding pattern (**8a,b**).

This bonding arrangement also satisfies the electron count ($2n + 2$ electrons) needed for *closo*-structures.[15] In **6**, this has been achieved by the participation of all the four valence electrons of one Si atom (Si$_{in}$) and two valence electrons of the other Si (Si$_{out}$) for skeletal bonding. There is another structure (**11**) on the HF potential energy surface corresponding to two lone pairs, one on each Si atom. Structure **11** is 9 kcal/mol higher in energy than **5**, with an Si−Si distance of 2.604 Å but without any bonding interaction. However, **11** is a third-order stationary point at the HF level. This structure may become more important for the heavier analogs. It collapses to **5** at the B3LYP level.

In view of the reactivity and novel bonding characteristics, **6** is an exciting target for experiments.

(14) Colegrove, B. V.; Schaefer, H. F., III *J. Phys. Chem.* **1990**, *94*, 5593.

(15) (a) Jemmis, E. D. *J. Am. Chem. Soc.* **1982,** *104,* 7017. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (c) Williams, R. E.; Gerhart, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513.