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Isolobal analogy between trivalent boron and divalent silicon

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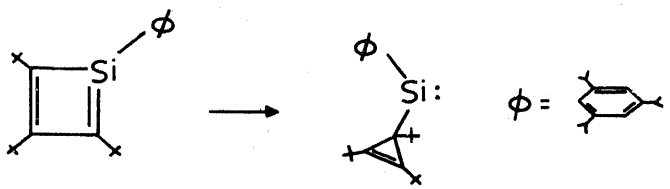
Abstract. Singlet organosilylenes with a lone pair and an empty *p* orbital are isolobal to trivalent borane if a B–H is equated to the lone pair on Si. Using this analogy, a particular isomer of CSi_2H_2 (24) is predicted to be a stable structure. MNDO calculations on 24 and many of its possible isomers suggest that 24 is at global minimum on the potential energy surface of CSi_2H_2. *Ab initio* calculations, using a minimal STO-3G basis set, on some selected structures also support these results.

Keywords. Isolobal analogy; trivalent borane; divalent silicon; MNDO calculations.

1. Introduction

Unlike carbenes, silylenes are shown to have thermal stability. The thermal isomerization of photogenerated 1-(2, 4, 6-triisopropylphenyl)-2, 3, 4-tri-*tert*-butyl-1-silacyclobutadiene (A) to (2, 4, 6-triisopropylphenyl) (1, 2, 3-tri-*tert*-butyl-cyclopropenyl) silylene (B) (Puranik and Fink 1989) clearly shows that the chemistry of silylene is different from that of carbenes. Even though silylenes such as $SiCl_2$ and SiF_2 (Atwell and Weynberg 1969; Bock *et al* 1985) are highly reactive, many silylenes especially with organic substituents are very stable in their singlet ground states (Schaefer 1982; Pearsall and West 1988). The divalent structures are preferred even when the alternative tetracoordinated Si structures are possible (Schaefer 1982). There



A B

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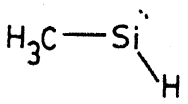
are several examples that illustrate the preference of silicon to be divalent. Thermochemical evidence (Shin *et al* 1988) shows that the heats of formation of methylsilylene (1) and silaethylene (2) are comparable (the difference is only 10 kcal/mol). Various theoretical studies also support this observation and point out that 2 is more stable than 1 only by about 4 kcal/mol (Grev *et al* 1988). 3 is calculated to be more stable than silaacetylene 4 (Murrell *et al* 1977; Hoffmann *et al* 1983). Hydroxysilylene (*trans*) (5) is lower in energy in comparison to silaketone (6) by 4·9 kcal/mol at the 6–31G* level (Kudo and Nagase 1984; Tachibana *et al* 1986). Aminosilylene (7) is found to be the global minimum on the potential energy surface of $NSiH_3$ (Truong and Gordon 1986). The corresponding silaimine isomer (8) is at least 18 kcal/mol higher in energy. Similarly 9 is more stable than 10 (Luke *et al* 1986). Apart from these, isomers with one or more silylene units are found either as the global minimum or close to it for many organosilicon compounds. For example, 2-methylcycloprop-2-ene-1-silylene is shown to be the global minimum on the potential energy surface of C_3SiH_4 (Shriver *et al* 1987). The fact that disilaacetylene is not a local minimum but leads to disilylene (Luke *et al* 1986) also suggests the stability of



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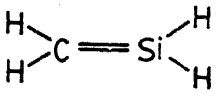

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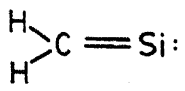

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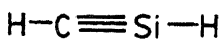

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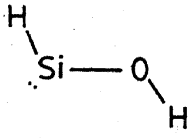

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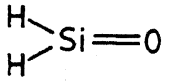

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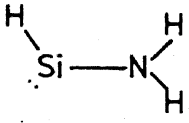

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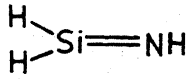

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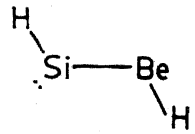

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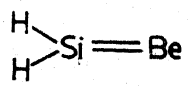
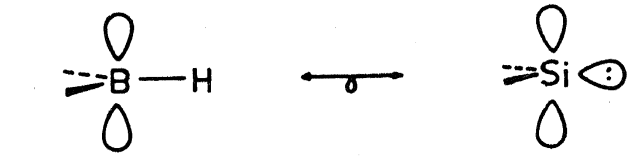


10

silylene compounds. These are all surprising results because the carbon analogs of each of these show a large preference for the tetravalent arrangement. Here we present an analogy between divalent silicon and trivalent boron which suggests that divalent Si compounds should actually be compared to trivalent boron compounds. This analogy also helps us in arriving at unusual silicon compounds based on structures of boron compounds. The semi-empirical MNDO method is used for calculating the structures and energies of various isomers discussed. Each minimum energy structure has been verified to be a true minimum.

2. Isolobal analogy between $H–BH_2$ and $:SiH_2$

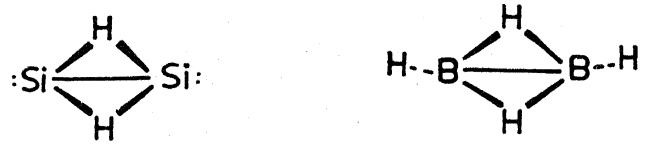
The simplest electronic structure description of divalent singlet silylene (12) involves two orbitals on silicon in addition to the two covalent bonds. One of them (a_1) is occupied with two electrons and the other (b_2) is empty (labels are according to the C_{2v} point group). Though it is not strictly isolobal (Hoffmann 1982), we propose an analogy between $H–BH_2$ (11) and $:SiH_2$(12). It may be possible to treat 11 and 12 as isolobal if the a_1 lone pair on 12 is taken as equivalent to the B–H bond in 11. Similarly, divalent Si and the B–H group may be considered isolobal. The diagonal



11 12

13 14

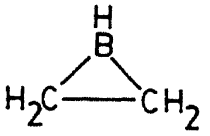
15 16



17 18

relationship in the periodic table also suggests similarities between boron and silicon, e.g., they have comparable electronegativities, ionization potentials (Greenwood and Earnshaw 1984; Cotton and Wilkinson 1988) and related characteristics.

The structural preferences shown by compounds containing trivalent boron and divalent silicon also support the proposed isolobal analogy. For example, among the isomers of Si_2H_2, 13 is found to be more stable than 14 (Luke *et al* 1986), and among the isomers of B_2H_4, 15 is more stable than 16 (Vincent and Schaefer 1981). Similarly both 17 (Luke *et al* 1986) and 18 (Mohr and Lipscomb 1986) are shown to be local minima. In fact, 17 is the global minimum on the PE surface of Si_2H_2. Both 19 (Krogh-Jespersen *et al* 1981) and 20 (Lien and Hopkinson 1981) are calculated to be stable structures. 21 (Krogh-Jespersen *et al* 1981) and 22 (Frenking *et al* 1986) are shown to have strong 2π electron delocalization and are global minima on their respective potential energy surfaces. While these provide striking similarities between structures involving Si or the BH group, to our knowledge, such an analogy between trivalent boron and divalent silicon has never been pointed out. Each of the experimental and theoretical observations have been rationalized in boron or silicon compounds individually. In this paper we introduce the isolobal analogy that exists between the divalent silicon and trivalent boron species and use this analogy to arrive



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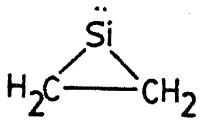

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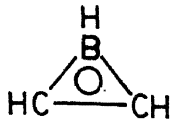

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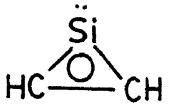

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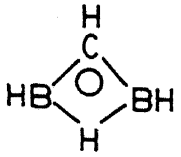

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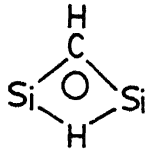

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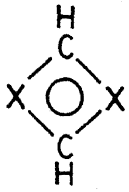
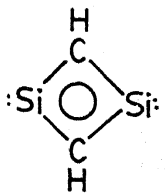


25 a b c

X = BH CH^+ Be



26

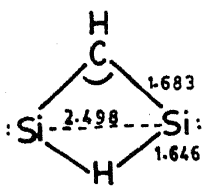
at unusual compounds of silicon. Some of the unconventional structures that we arrive at using the replacement of B–H units by silicon turn out to be the most stable isomers of the given molecular formulas.

Structures represented by the molecular formula, CSi_2H_2, are dealt with in detail in the present paper. The molecular formula CSi_2H_2 was selected from the stable structure 23 calculated for CB_2H_4 (Krogh-Jespersen *et al* 1979). Replacement of two BH groups by Si leads to 24. Even though various alternatives are studied for 24, this is found to be the global minimum in our study. It is possible to arrive at indefinitely large sets of compounds from the corresponding boranes. Another structure of current interest is $C_2Si_2H_2$, which may be obtained from a series of isoelectronic structures 25. 25a and 25b have been studied experimentally and theoretically (Budzelaar *et al* 1985); 25c is calculated to be a true minimum on the potential energy surface of $C_2Be_2H_2$ (Jug 1984). The new analogy between BH and Si enables us to suggest 26 as a stable arrangement for $C_2Si_2H_2$. However, we do not discuss the isomers of $C_2Si_2H_2$ here. The approach we present here to determine the structures of the silicon compounds lends itself to obvious extension.

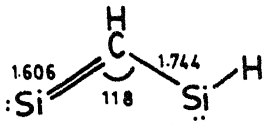
The electronic structures of the novel compound 24 and its isomers are studied using the MNDO method. The molecular orbital patterns and the relative stabilities of the isomers of 24 should facilitate further understanding of the proposed analogy. Silylenes are normally more stable in their singlet state (Balasubramanian and McLean 1986; Gordon and Bartol 1987) and hence the triplet structures are not studied. During the optimization no symmetry restrictions are imposed, but the electronic structures of the isomers of 24 are analysed according to the closest possible symmetry. Some of the isomers of 24 are also optimized at the *ab initio* level using a minimal STO–3G basis set (Hehre *et al* 1969, 1970) using the Micromol program (Colwell *et al* 1984). All calculations reported here have been carried out using a personal computer, PC AT.

2.1 *Structure and stabilities of the isomers of CSi_2H_2*

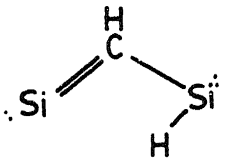
Figure 1 gives several possible structural isomers of CSi_2H_2, (24, 27–39). The relative energies are given after the serial number below each structure. Structures involving divalent carbene carbon atoms are not considered in the study because these are known to be very high energy species. Distinct groups of isomers emerge from these relative energies. Structures with both Si atoms occupying divalent positions are the most stable ones. Next come the structures with one divalent Si. We shall consider structures with two divalent Si atoms first (24, 27–34). Among these, structures with one three-membered ring (33, 34) are high in energy. Structures in which three-membered ring strain is released by a hydrogen bridge (24) or a ring-opened structure as in 27 are found to be very low in energy. 28 is not a local minimum, but on complete optimization becomes 24. 32 is also not a local minimum, but leads to 30 on optimization. All the structures with two divalent silicons and without a three-membered ring 24, 27–31 have 2π electron delocalization. This, in addition to strain, probably is the reason why these structures are more stable than those with three-membered rings, 33 and 34. Of all these, 24 – C_{2v}, is the most stable isomer. The Si–C bond length in 24 is 1·683 Å. This is in-between the standard MNDO Si–C single bond (1·800 Å) and the Si=C (1·642 Å) (Dewar *et al* 1986), indicating substantial double bond character. The electronic structure 24 clearly shows that the hydrogen



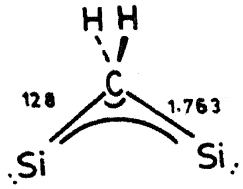
24, 0·0
(**24a**, 4·21)



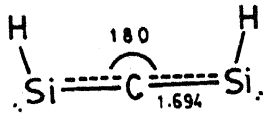
27, 16·52
(**27a**, –)



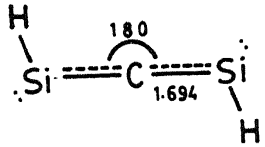
28
(**28a**, –)



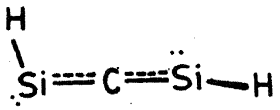
29, 112·61
(**29a**, 65·53)



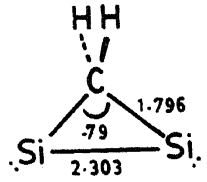
30, 52·31
(**30a**, 0·0)



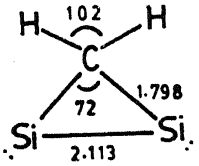
31, 54·12
(**31a**, 0·0)



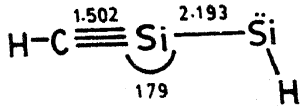
32
(**32a**)



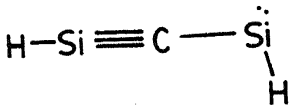
33, 50·83
(**33a**, 34·81)



34, 58·61
(**34a**, 31·32)



35, 84·33
(**35a**, 50·84)



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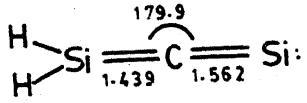
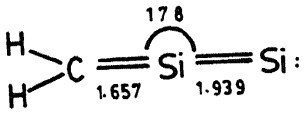


37, 60·74



38, 77·62

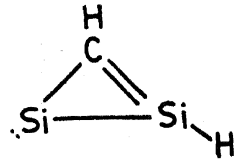


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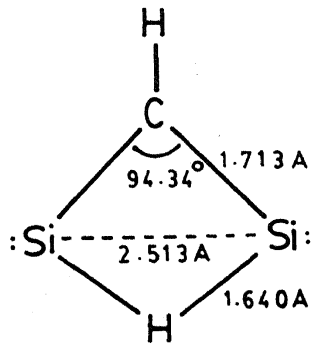
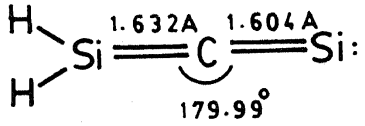
Figure 1. Calculated geometric parameters of the isomers of CSi_2H_2 using MNDO 1 method (distances in ångstroms and angles in degrees).

bridges the two Si atoms in a closed $3c$–$2e$ interaction (HOMO + 2), the Si–H distance being 1·646 Å. With a distance of 2·493 Å the Si–Si sigma bond is only slightly weakened by the bridging hydrogen. The three σ bonds around carbon (C–H, 2Si–C) leave one electron in the p orbital. The bridging hydrogen provides the second electron in the 2 electron delocalization of the π framework (HOMO). This is similar to other 2π aromatic systems such as cyclopropenyl cation. Scheme 1 gives the STO–3G results for 24. Calculations at the STO–3G level also support these MNDO

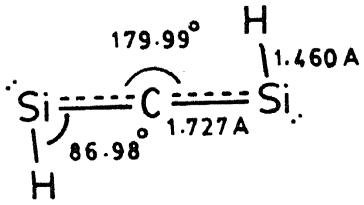


Relative Energies (Kcal/mol)

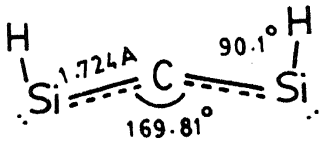
	STO-3G	MNDO
	0.00	0.00



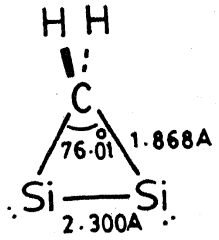
	STO-3G	MNDO
	43.12	60.74



	STO-3G	MNDO
	51.55	54.12



	STO-3G	MNDO
	51.92	52.31



	STO-3G	MNDO
	17.15	50.83

Scheme 1.

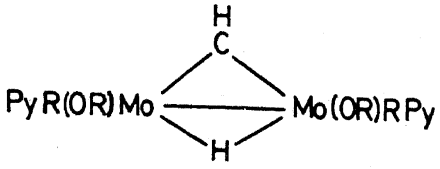
results. Even though neither the MNDO nor the STO–3G results are definitive, the large difference in the relative energies suggests that these results may not be dramatically changed at the higher levels of calculations which we currently pursue.

The next best isomer, the open chain 27 is higher in energy by only 16·5 kcal/mol at MNDO level. This isomer has allyl 2π electron delocalization, as evidenced by distances and molecular orbitals. 29 has a π electron delocalization via the pseudo π CH_2 (group) orbital, but does not stabilize the structure to a large extent. 30 and 31 are planar with a $2\pi e$ delocalization in the perpendicular plane. The central carbon has an empty *p* orbital which is stabilized by its interaction with the lone pairs on Si and Si–H bonds.

Isomers with one divalent silicon are at least 60 kcal/mol higher in energy than the global minimum. 36 does not correspond to a local minimum; complete optimization leads to 30. The cyclic structure 39 also leads to 27 or 24 depending on the C–Si–H angle initially used.

The B–H analogs of 24, and 27 to 34 with the molecular formula CB_2H_4 (Collins *et al* 1976; Krogh-Jespersen *et al* 1979) are also studied for comparison. 24a is shown to be a local minimum, which is only 4·2 kcal/mol higher than the global minimum. (In this paper the B–H analogs of the isomers of 24 and 26 are represented by the same structural number with a suffix 'a' attached. Thus 24a is actually 23.) In CB_2H_4, 30a is the most stable isomer. It has a planar structure with all the hydrogens in one plane. This structure was not considered in the previous study (Krogh-Jespersen *et al* 1979; Collins *et al* 1976). It has only two electrons in the π framework (unlike $4\pi e$ in allene). The same is true in 30 (CSi_2H_2) also. But in 30a (CB_2H_4) the stabilization of the empty *p* orbital on carbon is stronger because of the hyperconjugation with BH_2 and it becomes the global minimum. Even though there are some differences in the energy-ordering, the expected trend is maintained in the two series CSi_2H_2 and CB_2H_4. Thus, the analogy developed earlier has enabled us to reach at an unusually stable organosilicon compound of the molecular formula CSi_2H_2.

A very closely related example to 23 and 24 is found in organotransition-metal chemistry, 40 (Coffindaffer *et al* 1983). This compound is considered to have a metal–metal bond bridged by a hydrogen atom and a CH group. The MHM arrangement is the equivalent of a 3*c*–2*e* bond, so prevalent in borane chemistry. Similarly, 23 and 24 may be considered as compounds in which the main group metals are bridged by CH and H. One of the most interesting aspects of these compounds 23, 24 is the bridging of the two elements (B, Si) by an electron-deficient hydrogen and an electron-rich CH group.



40

Conclusions

The isolobal analogy between trivalent borane and divalent organosilicon is clearly pointed out with the help of several examples. 24, which is predicted to be stable, is

found to be a global minimum on the potential energy surface of CSi_2H_2 at MNDO and STO–3G levels of theory. The 2π electron delocalization in 24 causes extra stabilization. The chemistry of divalent Si is no more unusual than the chemistry of the boranes.

Acknowledgements

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References

Atwell W H and Weynberg D R 1969 *Angew. Chem., Int. Ed. Engl.* **8** 469
Balasubramanian K and McLean A D 1986 *J. Chem. Phys.* **85** 5117
Bock H, Solouki B and Maier G 1985 *Angew. Chem., Int. Ed. Engl.* **24** 205
Budzelaar P H M, Krogh-Jespersen K, Clark T and Schleyer P v R 1985 *J. Am. Chem. Soc.* **107** 2773
Coffindaffer T W, Rothwell I P and Huffmann J C 1983 *J. Chem. Soc., Chem. Commun.* 1249
Collins J B, Dill J D, Jemmis E D, Apeloig Y, Schleyer P v R, Seeger R and Pople J A 1976 *J. Am. Chem. Soc.* **98** 5419
Colwell S M, Marshall A R, Amos R D and Handy N C 1984 Program MICROMOL, developed at the Department of Theoretical Chemistry, University of Cambridge
Cotton F A and Wilkinson G 1988 *Advanced inorganic chemistry* 5th edn (New York: Wiley Interscience)
Dewar M J S, Friedheim J, Grady G, Healy E F and Stewart J J P 1986 *Organometallics* **5** 375
Frenking G, Remington R B and Schaefer H F III 1986 *J. Am. Chem. Soc.* **108** 2169
Gordon M S and Bartol D 1987 *J. Am. Chem. Soc.* **109** 5948
Greenwood N N and Earnshaw A 1984 *Chemistry of elements* (Oxford: Pergamon)
Grev R S, Scuseria G E, Scheiner A C, Schaefer H F III and Gordon M S 1988 *J. Am. Chem. Soc.* **110** 7337
Hehre W J, Ditchfield R, Stewart R F and Pople J A 1970 *J. Chem. Phys.* **52** 2769
Hehre W J, Stewart R E and Pople J A 1969 *J. Chem. Phys.* **51** 2657
Hoffmann R 1982 *Angew. Chem., Int. Ed. Engl.* **22** 711
Hoffmann M R, Yoshika Y and Schaefer H F III 1983 *J. Am. Chem. Soc.* **105** 1084
Jug K 1984 *J. Org. Chem.* **49** 4475
Krogh-Jespersen K, Cremer D, Dill J D, Pople J A and Schleyer P v R 1981 *J. Am. Chem. Soc.* **103** 2589
Krogh-Jespersen K, Cremer D, Popinger D, Pople J A, Schleyer P v R and Chandrasekhar J 1979 *J. Am. Chem. Soc.* **101** 4843
Kudo T and Nagase S 1984 *J. Phys. Chem.* **88** 2833
Kutzelnigg W 1984 *Angew. Chem., Int. Ed. Engl.* **23** 266
Lien M H and Hopkinson A C 1981 *Chem. Phys. Lett.* **80** 114
Luke B T, Pople J A, Krogh-Jespersen M-B, Apeloig Y, Karni M, Chandrasekhar J and Schleyer P v R 1986 *J. Am. Chem. Soc.* **108** 270
Mohr R R and Lipscomb W N 1986 *Inorg. Chem.* **25** 1053
Murrell J N, Kroto H W and Guest M F 1977 *J. Chem. Soc., Chem. Commun.* 619
Pearsall M-A and West R 1988 *J. Am. Chem. Soc.* **110** 7228, and references therein
Puranik D B and Fink M J 1989 *J. Am. Chem. Soc.* **111** 5951
Schaefer H F III 1982 *Acc. Chem. Res.* **15** 283
Schriver G V, Fink M J and Gordon M S 1987 *Organometallics* **6** 1177
Shin S K, Irikura K K, Beauchamp J L and Goddard W A III 1988 *J. Am. Chem. Soc.* **110** 24
Tachibana A, Fueno H and Yamabe T 1986 *J. Am. Chem. Soc.* **108** 4346
Truong T N and Gordon M S 1986 *J. Am. Chem. Soc.* **108** 1775
Vincent M A and Schaefer H F III 1981 *J. Am. Chem. Soc.* **103** 5677