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The Boron Connection: A Parallel Description of Aromatic, Bonding, and Structural Characteristics of Hydrogenated Silicon−Carbon Clusters and Isovalent Carboranes

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The aromatic, bonding, and structural characteristics of the $Si_4C_2H_2-C_2B_4H_6$, $Si_2C_4H_4-C_4B_2H_6$, and other $Si_nC_2H_2-C_2B_nH_{n+2}$ ($n = 1, 2, 3, 5$) isovalent pairs are studied using density functional theory (DFT) and coupled cluster methods to fully illustrate the homology of the two species. This homology, which is based on the replacement of the carborane B−H units by isovalent Si atoms, is extended to all three characteristics (structural, electronic, and aromatic) and includes all three lowest-energy structures of the isovalent pairs. This type of "boron connection", which has been tested for silicon clusters recently, seems to be a valid and extremely useful concept. For the aromatic properties of the $Si_nC_2H_2-C_2B_nH_{n+2}$ species, expressed through the nucleus independent chemical shifts (NICS), a strange odd−even effect with respect to the number of Si atoms is observed which seems rather difficult to explain. To help possible future identification and characterization of the $Si_nC_2H_2$ clusters, their infrared, Raman, and optical excitation spectra are calculated within the framework of DFT, using the 6-311+G(2d, p) basis set. It is expected that the present results would facilitate the exploitation of the well-known carborane and metallacarborane chemical properties and applications for the design and development of novel silicon−carbon-based composite materials.

I. Introduction

The structural chemistry of boranes and carboranes is a very rich and well-established branch of chemistry which reached its highest point more than 30 years ago with the development of well-known and, over the years, well-tested structural and stability rules.[1−5] Numerous important concepts of theoretical chemistry, such as fluxional molecular rearrangements (and isomerization,[1,2] well-known from organic chemistry), multicenter bonding,[1,2] and three-dimensional aromaticity,[6,7] have evolved from the study of boranes and carboranes. On the other hand, the field of SiC (and Si) clusters, which is also mature enough, is lacking such general stability criteria and concepts, although some general building up principles and concepts were put forward by the present author and collaborators, almost 15 years ago.[8,9] Multicener bonding and alternating charges[8−10] are among the building up criteria for SiC clusters, which are also fundamental for organometalic carboranes[1,4] and boranes. Therefore, it would be very interesting to examine whether or not a more general relation could be established with carboranes and suitably chosen isovalent SiC clusters. In favor of such a relation is the "homology" recently

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illustrated by the present author[11,12] for silicon clusters Si_n and cluster dianions Si_n^{2-} with the corresponding isovalent boranes B_nH_n and $B_nH_n^{2-}$. This type of connection, which could be loosely called boron connection part 1, is on top of the well-known Si−B (similar to Li−Mg and Be−Al) diagonal relationships, described in chemistry textbooks. Such diagonal relationships, in particular for size-related properties, between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table are practically due to the simple fact that the atomic size of an element increases down a group and decreases across the period, the two effects tending to cancel each other. As a result of the diagonal relationship, boron and silicon are both semiconductors; they form halides that are hydrolyzed in water and have acidic oxides.

The $B_nH_n^{2-}/Si_n^{2-}$ similarity on the other hand is practically based on the formal replacement of a BH^{2-} subunit with an isovalent Si^{2-} dianion,[11] which in several cases can be stretched up to a B_nH_n/Si_n similarity.[12] The idea of connecting the structural chemistry of B_nH_n and Si_n clusters (in a rather different context) goes back to Mingos and collaborators[13] and Walles,[14] as the author became aware recently.[15]

This simple "replacement rule" in the case of closo carboranes of the form $C_2B_nH_{n+2}$ leads to isovalent hydrogenated silicon−carbon clusters of the form $Si_nC_2H_2$. This is also true for the $Si_4C_2H_2$−$C_4B_2H_6$ pairs. As will be illustrated bellow, these hypothetical (since they have not as yet been synthesized or characterized) silicon carbon clusters have remarkable structures in full analogy to the well-known structures of the corresponding closo carboranes.

Here, we examine, in addition to structural similarities, bonding and aromatic similarities (homologies) between these isovalent species. The similarities are remarkable and can be possibly used in the future for the design of more complex (self-assembled) materials in analogy to carborane complexes used as building blocks for new materials (see for instance ref 16).

Furthermore, on the basis of the calculated infrared (IR) spectra, it is reasonable to expect that such clusters could be present in relatively large abundances in circumstellar space (see refs 17 and 18 for alternative assignments of the corresponding stellar IR lines), similarly to bare SiC clusters.[19] Such hydrogenated SiC clusters can probably be synthesized and studied with methods similar to the methods used for hydrogenated silicon clusters[20] and fulleranes.[21]

The remarkable similarities in structural, bonding, and aromatic characteristics revealed here are present not only for the lowest energy but also for the second- and third-lowest energy structures of all $Si_nC_2H_2$−$C_2B_nH_{n+2}$, $n = 1-5$, and $Si_4C_2H_2$−$C_2B_4H_6$ homologous pairs. It is therefore realistic to suggest that these new hydrogenated silicon carbon clusters constitute a new class of clusters. Judging from the cases examined here, these hydrogenated clusters would be very stable (with atomization energies almost double, compared to the corresponding non-hydrogenated Si_nC_2 clusters) and have large highest occupied molecular orbital−lowest unoccupied molecular orbital gaps.

The present paper is organized as follows: After the technical details of the calculations in the next section (II), the results of the calculations for $Si_nC_2H_2$−$C_2B_nH_{n+2}$, $n = 1-5$, pairs are presented and discussed in section III. In section IV, the $Si_4C_2H_2$−$C_2B_4H_6$ results are analyzed. Finally, the main conclusions and findings of the present work are summarized in section V.

II. Computational Details

The calculations for all structures, initial and final geometries and optimizations, were first performed within density functional theory (DFT), using the hybrid exchange and correlation functional of Becke/Lee, Parr, and Yang (B3LYP)[22] and the triple-ζ valence polarized (TZVP) basis set.[23] At the B3LYP/TZVP geometry, population analysis was performed using both Mulliken and the Roby−Davidson−Heinzmann−Ahlrichs method[24] of population analysis, in which the bonding features are described by the shared electron numbers (SENs) for two-, three-, and four-center bonds. These calculations were performed with the TURBOMOL program package.[25] At this geometry, the excitation spectrum of the lowest-energy clusters was calculated using the time-dependent DFT (TDDFT) method with the B3LYP functional and the TZVP basis set, as implemented in the TURBOMOL package.[25] Subsequently, the lower-energy structures were further optimized with the coupled-cluster method, including single and double excitations (CCSD), while the final energies were recalculated at the CCSD(T) level, which in addition includes in a perturbative way the triple excitations (T). All of these calculations were performed with the Gaussian program package,[26] using the 6-311+G(2d, p) basis set, as implemented in this package.[26] The same package was also used for the calculation of the nucleus independent chemical shift (NICS) values and the nuclear magnetic resonance (NMR) chemical shifts of the individual atoms, using the gauge independent atomic orbital method.

III. Results and Discussion for the $Si_nC_2H_2$−$C_2B_nH_{n+2}$, $n = 1-5$, Pairs

A. Comparison of Structural Properties. The three lowest-energy structures of $Si_nC_2H_2$ and $C_2B_nH_{n+2}$, $n = 1-5$,

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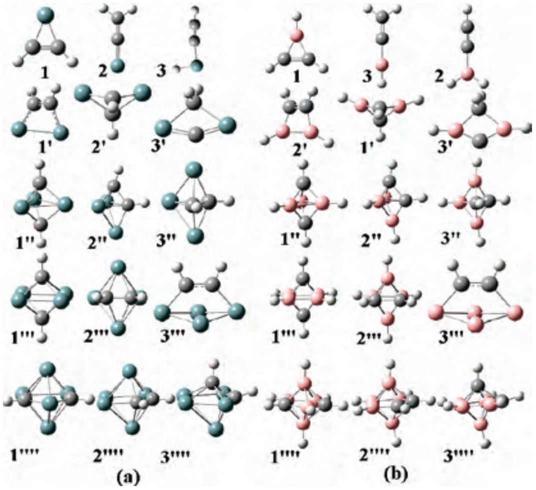

Figure 1. (Color on line) The three lowest-energy structures of $Si_nC_2H_2$ clusters on the left (a) and the corresponding homologous carboranes $C_2B_nH_{n+2}$, $n = 1-5$, on the right (b). The numbers (with and without primes) denote the energetic ordering of the homologous species in each horizontal row of structures.

are shown in Figure 1. All of these structures are true minima of the energy hypersurface, with real vibrational frequencies (see the Supporting Information). Since a large number of alternative structures and geometry optimizations (symmetry constrained and unconstrained) have been considered and examined, it could be expected that these (or most of these) structures could be global minima. As we can see in this figure, the structural similarity between the two species is amazing. One by one, the three lowest-energy structures are fully homologous. In two (borderline) cases, $n = 1$ and 2, the energy ordering of the second- and third-lowest (for $n = 1$) or the lowest and second-lowest (for $n = 2$) has been reversed.

In the $n = 1$ case, the reason is simply the stronger impact (higher strength) of the C−H interaction compared to Si−H (partial saturation of the dangling bond). For the same reason, in all cases examined here ($n = 1-5$), the lowest-energy structures always correspond to hydrogens attached to two carbon atoms. Second in preference is the attachment onto the same carbon atom (with the third preference, one on carbon and one on Si). In the case of $Si_2C_2H_2$, the relative strength of the C−C compared to Si−C bonds is the decisive factor for the stabilization and the energy ordering, similarly to bare SiC clusters.[8−10]

The "puckering" of the two lowest-energy (nonplanar) structures (of both $Si_2C_2H_2$ and $C_2B_2H_4$) is apparently due to the optimization of sp^3 bond angles.[18] The puckering tendency is larger in $Si_2C_2H_2$ compared to $C_2B_nH_4$. Contrary to the border cases ($n = 1$, 2), for $n = 3-5$, the energetic ordering is exactly the same for both species. For $n = 3$, the energetic ordering of the double-primed structures in the third row of Figure 1, which all originate from the trigonal bipyramid of Si_5^{2-} and $B_5H_5^{2-}$, is exactly the same for both species. As a matter of fact, this ordering is in full accord with the empirical valence rules[27] and topological charge stabilization[28] concepts developed for carboranes. These rules demand that the structure obtained by the (1,5) substitution of two Si atoms by C (and hydrogenation) is the most stable one. The same structure is also the most symmetric, characterized by the full D_{3h} symmetry[12] of Si_5^{2-} and $B_5H_5^{2-}$. The second-lowest-energy structures are obtained by (1,2) substitution, whereas the third-lowest-energy structures are characterized by (2,3) substitutions. Similarly, the two lowest-energy structures in the fourth row of Figure 1 are obtained from the octahedral structure of Si_6^{2-} (and $B_6H_6^{2-}$) dianions by (1,6) and (2,3) substitutions. Due to the underlying O_h symmetry, the (1,2) and (2,3) substitutions are equivalent. Here again, the most symmetric (1,6) structure characterized by D_{4h} symmetry is the most stable. This is not necessarily the rule for all cases. As we can see in the fifth row of Figure 1, the lowest-energy isomer for $n = 5$ is not the (1,7) isomer characterized by the full D_{5h} symmetry of the Si_7^{2-} (and $B_7H_7^{2-}$) dianions, but the (2,4)- C_{2v} symmetric isomer. This is also true for the corresponding carborane(s) and is fully consistent with the empirical valence[27] and topological charges stabilization rules[28] mentioned above.

B. Comparison of Bonding Properties. The basic bonding characteristic of both carboranes and SiC clusters is multicenter bonding, which can be quantified through two-, three-, and four- center SENs.[24] The SEN values for the lowest-energy structures of the two species are shown in Table 1. For $n = 2$, where the ordering of the lowest- and second-lowest-energy structures of $Si_2C_2H_2$ and $C_2B_2H_4$ is reversed, SENs are given for both the C_2-symmetric, which is the lowest-energy structure of $Si_2C_2H_2$, and the C_{2v} lowest-energy structures of $C_2B_2H_4$. As we can see in Table 1, although the three- and four-center SENs are slightly larger in the C_{2v} structure, the two-center C−C and Si−Si bonds are much stronger in the C_2 structure. Also, the two two-center Si−C bonds are stronger in the C_2 isomer. However, in the C_{2v} isomer, there are four Si−C bonds compared to two (and two "half bonds" with SEN = 0.59) in the C_2 isomer.

Furthermore (and most important), as we can see in Table 1, the SEN values for the lowest-energy structures of all isovalent pairs are fully homologous (with the SEN values in carboranes being somewhat larger). Thus, the structural homology is also associated with (multicenter) bonding homology, as would be expected.

C. Comparison of Aromatic Properties. In order to compare the aromatic character of both species, we need a

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Table 1. Two-, Three-, and Four-Center SEN for the Lowest-Energy Structures of $Si_nC_2H_2$ and $C_2B_nH_{n+2}$ ($n = 1-5$) Obtained by the B3LYP/TZVP Method[a]

N	$Si_nC_2H_2$	$C_2B_nH_{2n+2}$
1	C(1)C(2) 2.27	C(1)C(2) 2.10
	C(1)Si(3) 1.83	C(1)B(3) 2.02
	C(1)C(2)Si(3) 0.60	C(1)C(2)B(3) 0.62
2 C_{2v}	C(1)C(2) 1.14	C(1)C(2) 0.92
	C(1)Si(3) 1.74	C(1)B(3) 1.88
	Si(3)Si(4) 0.24	B(3)B(4) 0.62
	C(1)C(2)Si(3) 0.43	C(1)C(2)B(3) 0.39
	C(1)Si(3)Si(4) 0.15	C(1)B(3)B(4) 0.31
	C(1)C(2)Si(3)Si(4) 0.12	C(1)C(2)B(3)B(4) 0.08
2 C_2	C(1)C(2) 1.90	C(1)C(2) 1.94
	C(1)Si(3) 0.59	C(1)B(3) 0.65
	C(1)Si(4) 1.89	C(1)B(4) 1.86
	Si(3)Si(4) 1.41	B(3)B(4) 1.81
	C(1)C(2)Si(3) 0.28	C(1)C(2)B(3) 0.32
	C(1)Si(3)Si(4) 0.29	C(1)B(3)B(4) 0.32
3	C(1)Si(2) 1.55	C(1)B(2) 1.68
	Si(2)Si(3) 0.71	B(2)B(3) 0.99
	C(1)Si(2)Si(3) 0.33	C(1)B(2)B(3) 0.44
	C(1)Si(2)Si(3)Si(4) 0.05	B(2)B(3)B(4) 0.06
		C(1)B(2)B(3)B(4) 0.07
4	C(1)Si(2) 1.24	C(1)B(2) 1.40
	Si(2)Si(3) 1.25	B(2)B(3) 1.31
	C(1)Si(2)Si(3) 0.34	C(1)B(2)B(3) 0.45
	C(1)Si(2)Si(4)C(6) 0.05	C(1)B(2)B(4)C(6) 0.07
	Si(2)Si(3)Si(4)Si(5) 0.13	B(2)B(3)B(4)B(5) 0.06
5	Si(1)C(2) 1.10	B(1)C(2) 1.12
	C(2)Si(6) 1.30	C(2)B(6) 1.52
	C(2)Si(5) 1.46	C(2)B(5) 1.52
	Si(5)Si(6) 1.21	B(5)B(6) 1.69
	Si(1)Si(3) 0.84	B(1)B(3) 1.25
	Si(1)Si(6) 0.96	B(1)B(6) 1.11
	Si(1)C(2)Si(3) 0.33	B(1)C(2)B(3) 0.36
	S(1)Si(5)Si(6) 0.32	B(1)B(5)B(6) 0.53
	Si(1)C(2)Si(5) 0.32	B(1)C(2)B(5) 0.33
	Si(1)C(2)C(4)Si(6) 0.05	B(1)B(3)B(4)B(6) 0.06
	C(2)C(4)Si(5)Si(6) 0.06	B(3)B(5)B4(5)B(6) 0.06

[a] Only SEN values larger than 0.05 are listed. SEN values on symmetry equivalent atoms are not shown.

Table 2. Comparison of the NICS(0) Values of the Lowest-Energy Structures (in ppm) Obtained at the B3LYP/6-311+G(2d,p) Level of Theory

SiC_2H_2	$Si_2C_2H_2$	$Si_3C_2H_2$	$Si_4C_2H_2$	$Si_5C_2H_2$
−10.7	−13.7	−7.2	−13.8	−7.3
CB_2H_3	$C_2B_2H_4$	$C_2B_3H_5$	$C_2B_4H_6$	$C_2B_5H_7$
−20.4	−21.4	−15.3	−29.5	−23.6

measure of (three-dimensional) aromaticity through the usual aromaticity indices.[6,7] One of the best known aromatic indices is the NICS[7] usually evaluated at the center of the molecule (origin), NICS(0). The values of NICS(0) in parts per million for all five pairs of homologous species are listed in Table 2. As we can see in Table 2, the aromatic behavior of both species is similar. All NICS(0) values are diatropic (negative), which is characteristic of aromatic behavior. These clusters, and in particular the $n = 3$, 4, and 5 ones, are three-dimensional polyhedral (trigonal bipyramids, octahedral, etc.) structures characterized by three-dimensional aromaticity. The corresponding carboranes and the homologous $Si_nC_2H_2$ clusters are three-dimensional σ aromatics, except the first two members of the group $n = 1$ and 2, which are border cases. The planar SiC_2H_2 three-membered ring ($n = 1$), in full analogy to C_2BH_3 (borirene), is characterized by planar π aromaticity. The simplest way to illustrate this is by considering, in addition to NICS(0), the NICS(1) value, which is obtained by calculating NICS at a point 1 Å above the center of the ring. For planar π aromatics, it is expected that the NICS(1) value would be "more aromatic" (more negative) compared to NICS(0), reflecting the π-electron toroid densities. Indeed, the calculated NICS(1) value for SiC_2H_2, at the B3LYP/6-311+G(2d,p) level of theory, is −12.7 ppm. This value is clearly "more aromatic" than the −10.7 ppm NICS(0) value, calculated at the same level of theory.

The puckered $Si_2C_2H_2$ and $C_2B_2H_4$ four-membered structures are in the border between planar π and three-dimensional σ aromaticity. These isomers are characterized by (nonplanar) π and σ aromatic components, the percentages of which are different in the two different species.

The trends in the variation with n (the number of Si or B atoms) of "aromaticity" for both species is the same, although the NICS(0) values of $Si_nC_2H_2$ are about half the values of $C_2B_nH_{n+2}$, for $n = 1-5$. This must be related to partial σ antiaromaticity of the Si subunits in $Si_nC_2H_{n+2}$, which for the Si cluster dianions is known to be stronger for high-symmetry structures.[11,12,29] For the same reason, the NICS(0) value of the high-symmetry (O_h) Si_6^{2-} dianion turns out to be positive, although the corresponding value for isovalent $B_6H_6^{2-}$ borane is clearly negative, due to the reverse ordering of the t_{1u} and t_{2g} orbitals in Si_6^{2-} relative to the case of $B_6H_6^{2-}$ (see ref 12) and the domination of paratropic orbital contributions to the NICS(0) value.[29]

Finally, looking at the $Si_nC_2H_2$ NICS(0) values in Table 2, as a function of n, we can notice an odd−even effect, which taken literally (assuming it holds true for larger clusters) seems to indicate stronger aromaticity for the clusters with an even number of Si atoms and weaker aromaticity for odd Si number clusters. This includes the π-aromatic SiC_2H_2 cluster and is almost true for the corresponding carboranes, with the exception of $C_2B_5H_7$, which has a more negative NICS(0) value compared to $C_2B_2H_4$. There is no obvious explanation for this effect, which is not associated with a corresponding odd−even stability effect, or with obvious trends in the individual atomic NMR chemical shifts (given in the Supporting Information). Apparently, the relative magnitude of the aromatic relative to antiaromatic σ contributions should be different for odd and even Si numbers. One possible explanation could be that an even number of Si atoms might favor the formation of planar (or almost planar) silicon ring subunits. This could be illustrated by comparing the lowest-energy structures of $Si_4C_2H_2$ and $Si_5C_2H_2$ in Figure 1. In $Si_4C_2H_2$, contrary to $Si_5C_2H_2$, all Si atoms are in the same plane. This is reminiscent of the odd−even alteration in stability of C rings in comparison to linear structures of small carbon clusters. It would be interesting to test this effect for larger n clusters. In this case, if this effect holds true, one would expect the formation of more Si-ring subunits for the even n clusters.

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(29) King, R. B.; Heine, T.; Corminboeuf, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2004**, *126*, 430.

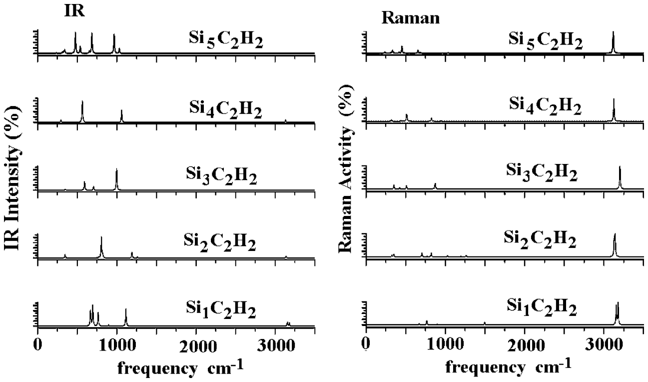

Figure 2. The IR (left) and Raman (right) spectra of the lowest-energy $Si_nC_2H_2$, $n = 1-5$, clusters.

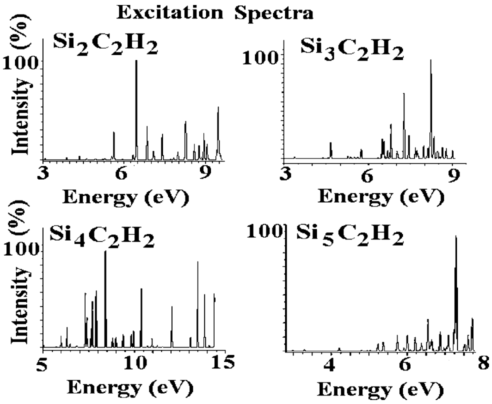

Figure 3. The excitation spectra of the $Si_nC_2H_2$, $n = 2-5$, clusters.

D. Characterization Properties. A more detailed study of the small $Si_nC_2H_2$ clusters is published elsewhere.[30] Here, we summarize, in addition to aromatic, some spectral properties which could help future characterization and identification of these species if they can be synthesized. These properties include IR and Raman spectra, as well as excitation (or absorption) spectra.

1. IR and Raman Spectra. The IR and Raman spectra of the $Si_nC_2H_2$, $n = 1-5$, clusters are shown in Figure 2.

As we can see in this figure, all clusters have intense lines in the region of C−H bond bending modes around 1000−1200 cm^{-1}. At the same time, we can see that, although all of these clusters have IR-active modes with frequencies in the region of 3100 cm^{-1} (C−H bond stretching) observed in stellar IR emission, these frequencies with relative intensities of a few percent of the peak intensity are barely visible in the scale of the figure. On the other hand, at exactly the same region (around 3100 cm^{-1}), all (with no exception) clusters are characterized by a very high (the peak) Raman activity (intensity) mode.

2. Excitation Spectra. In Figure 3, the excitation spectra of the $Si_nC_2H_2$, $n = 2-5$, clusters are given as calculated with the TDDFT/B3LYP method. As we can see in the figure, contrary to the IR and Raman spectra, which present several general common features, these spectra are characteristic of the individual species, without any obvious similarities.

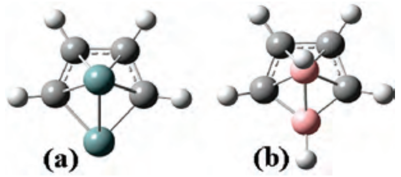

Figure 4. (Color on line) The lowest-energy structures of the $Si_2C_4H_4$ cluster (a) and the isovalent $C_4B_2H_6$ carborane (b).

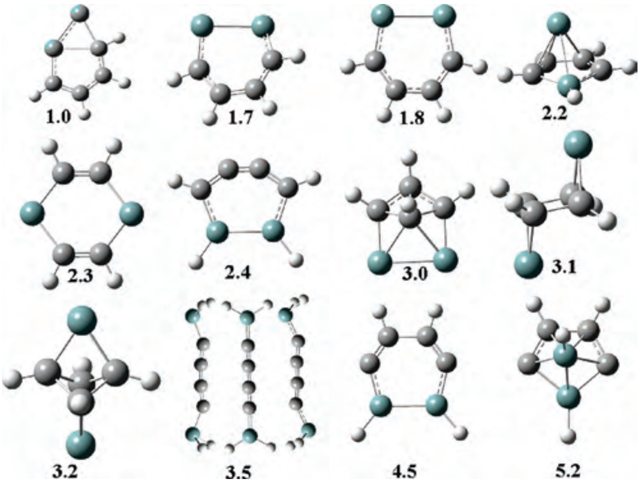

Figure 5. (Color on line) Higher-energy structures of $Si_2C_4H_4$. The structures are labeled according to their energy differences (in eV) from the lowest-energy structure (calculated at the B3LYP/6-311+G(2d, p) level of theory).

IV. Results and Discussion for the $Si_2C_4H_4-C_4B_2H_6$ Pairs

A. Structural and Energetic Properties. Figure 4 shows the lowest-energy structures of the pair $Si_2C_4H_4-C_4B_2H_6$. The similarity is amazing. The lowest-energy $C_4B_2H_6$ structure in Figure 4b is in full agreement with the results of Tian,[31] which are in agreement with experimental results (see ref 31). This structure, with C_s symmetry, is characterized as 2,3,4,5-$C_4B_2H_6$ and is isoelectronic to the B_6H_{10} borane.

The rest of the lower- and higher-energy (up to 5.2 eV) structures of $Si_2C_4H_4$ are shown in Figure 5, which also shows their energetic ordering and energy differences.

As we can see in Figure 5, the second-lowest-energy structure of $Si_2C_4H_4$ is a distorted planar ring of C_s symmetry 1 eV higher in energy. The corresponding carborane is 1.7 eV higher from the lowest-energy structure. Similarly to $Si_4C_2H_2$ and the other $Si_nC_2H_2$ clusters, the lowest- and next-lowest-energy structures have the hydrogens attached onto the carbon atoms. From Figure 5, we can see that the pyramidal structures similar to the ground state but with one and two hydrogens attached to one and two silicon atoms (in that order) are higher in energy by 2.2 and 5.2 eV, respectively. This is again in favor of the $Si_2C_4H_4-C_4B_2H_6$ homology, which is based on the replacement of B−H units by Si.

B. Comparison of Bonding Properties. As we have seen in the Introduction, the basic bonding characteristics of the carboranes (and the isovalent hydrogenated silicon−carbon

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(30) (a) Zdetsis, A. D. *J. Chem. Phys.* **2008**, *128*, 184305. (b) Zdetsis, A. D. *J. Phys. Chem. A* **2008**, *112*, 5712.

(31) Tian, S. X. *J. Phys. Chem. A* **2005**, *109*, 6580.

Table 3. One-Center Charges and Two-, Three-, and Four-Center SEN for the Lowest-Energy Structures of $Si_2C_4H_4$ and $C_4B_2H_6$[a]

$Si_2C_4H_4$	$C_4B_2H_6$
C(2), C(3) +0.04 (0.0)	C(2), C(3) +0.12 (+0.07)
C(4), C(5) −0.13 (−0.16)	C(4), C(5) +0.10 (+0.03)
Si(1) +0.59 (+0.19)	B(1) +0.43 (−0.03)
Si(6) −0.01 (−0.02)	B(6) −0.07 (−0.17)
C(2)C(3) 1.69; C(2)C(5) 1.73	C(2)C(3) 1.65; C(2)C(5) 1.60
C(2)Si(1) 0.88; C(4)Si(1) 0.95	C(2)B(1) 1.07; C(4)B(1) 1.18
C(4)Si(6) 1.48; Si(1)Si(6) 0.82	C(4) B(6) 1.69; B(1)B(6) 1.05
C(2)C(3)Si(1) 0.35; C(2)C(5)Si(1) 0.35	C(2)C(3)B(1) 0.36; C(2)C(5)B(1) 0.37
C(4)Si(1)Si(6) 0.28	C(4)B(1)B(6) 0.41
C(2)C(3)C(4)C(5) 0.04	C(2)C(3)C(4)C(5) 0.04
C(2)C(3)C(4)Si(1) 0.04	
C(3)C(4)C(5)Si(6) 0.04	C(3)C(4)C(5)B(6) 0.04
C(2)C(4)C(5)Si(6) 0.04	C(2)C(4)C(5)B(6) 0.03
C(2)C(4)C(5)Si(1) 0.02	C(2)C(4)C(5)B(1) 0.02

[a] Charges in parentheses are assigned after the multicenter bonding is taken care of. Only three-center SENs larger than 0.05 and four-center SENs larger than 0.02 are listed. SEN values on hydrogens and symmetry-equivalent atoms are not shown.

Table 4. Comparison of NICS(0) Values; Anisotropies, $\Delta\chi$; and Individual Atomic NMR Chemical Shifts, δ, in ppm

	$Si_2C_4H_4$	$C_4B_2H_6$
NICS(0)	−29.3	−27.3
$\Delta\chi$	−9.0	−7.8
$\delta(C_1)$	58.6	82.8
$\delta(C_2)$	53.5	93.4
δ(Si/B) top	737.3	167.2
δ(Si/B) basal	287.1	92.5

clusters) are multicenter bonding and alternating charges on the atoms. These characteristics are shown and compared in Table 3. The atomic charges in the top rows of Table 3 clearly illustrate the charge alteration (either for a loop going through the apex Si atom, Si(1), or through the basal Si(6) on the basal plane of the pyramid). This is true either for charges calculated after considering (only) two-center bonds or after multicenter bonding has been taken into account (charges inside parentheses in Table 3). The charge alteration is practically the same for both species and so is multicenter bonding. The amount of three-center bonding is slightly larger in the carborane, whereas the amount of four-center bonding is slightly larger in $Si_2C_4H_4$ (not counting the multicenter bonding involving hydrogen). We can also observe that two-center C−C bonding is somewhat stronger in $Si_2C_4H_4$. On the other hand, the Si−Si and Si−C bonds are slightly weaker compared to the B−B and B−C bonds.

C. Comparison of Aromatic Properties. As we have already seen, a synoptic description of aromatic properties is given through the NICS(0) aromaticity index. A more detailed description, which is also important for characterization, is given through the NMR chemical shifts of the individual atoms. The NICS(0) values and the (absolute) NMR chemical shifts of the individual atoms are listed and compared in Table 4. The absolute values, however, are not as useful as the relative values with respect to the tetramethylsilane (TMS) prototype molecule. The reference values of TMS for carbon, silicon, and boron, calculated at the same level of theory (B3LYP/6−311+G(2d,p)), are $\delta_{TMS}(C) = 182.47$, $\delta_{TMS}(Si) = 327.39$, and $\delta_{TMS}(B) = 83.6$ ppm, respectively. The NMR chemical shifts of silicon and carbon relative to TMS are given in Figures SI.1 and SI.2 in the Supporting Information.

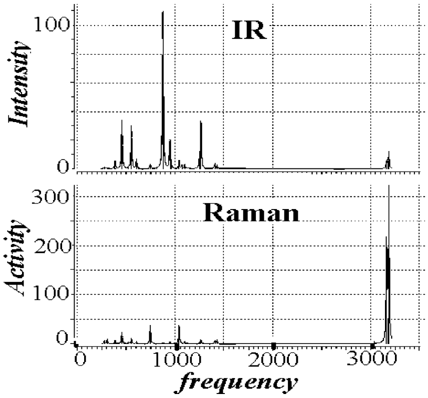

Figure 6. The IR (top) and Raman (bottom) spectra of the $Si_2C_4H_4$ cluster.

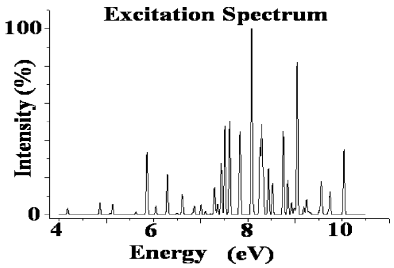

Figure 7. The excitation spectrum of $Si_2C_4H_4$.

From the NICS(0) values in Table 4, we can see that, contrary to the case of $Si_nC_2H_2$ clusters, the NICS(0) values of $Si_2C_4H_4$ are of equal magnitude and larger compared to the corresponding isovalent carborane.

This is apparently related to the larger number (four) of carbon atoms in the basal plane. However, the planarity of the carbons is not such a crucial factor, as can be verified by the fact that the NICS(0) value of the second-lowest-energy planar structure of $Si_2C_4H_4$ is considerably smaller (−19.3 ppm). This could be considered as an additional hint that the (3D) aromaticity is of σ type, as for the $C_2B_nH_{2n+2}$ carboranes. The large difference in the NMR chemical shifts of basal and apex silicon (and boron) atoms in Table 4 verify the different chemical environment of these atoms.

Similarly, the small differences of chemical shifts of carbon atoms reflect the different chemical environment of carbons (carbons bonded to two carbons and carbons bonded to both silicon and carbon). The same values also verify the full homology (similar chemical environment) of the carbons in $Si_2C_4H_4$ and $C_4B_2H_6$; the difference of chemical shifts between the two is on the order of 30 ppm.

D. Characterization Properties. 1. IR and Raman Spectra. Similarly to the $Si_nC_2H_2$ clusters, in Figure 6, the IR and Raman spectra of $Si_2C_4H_4$ are shown to help possible future characterization. As in the case of $Si_nC_2H_2$ clusters, the IR spectrum has a weak (about 10% of the peak intensity) but sharp line at about 3100 cm^{-1}. At the same frequency, the Raman spectrum shows its peak intensity.

2. Excitation Spectrum. The excitation spectrum of $Si_2C_4H_4$ is shown in Figure 7.

As in the case of $Si_nC_2H_2$ clusters, this spectrum has no obvious similarities with other similar species. When compared with $Si_4C_2H_2$, we can notice the maximum intensity peak around 8 eV and a secondary peak at 10 eV, which are common in both species.

V. Conclusions

It has been verified that the $Si_nC_2H_2$ clusters for $n = 1–5$, and presumably for larger values of n are fully homologous (structurally, electronically, and aromatically) to the corresponding isovalent carboranes $C_2B_nH_{n+2}$ ($n = 1, 2, 3, 4, 5$). This homology is totally extended to the $Si_2C_4H_4$−$C_4B_2H_6$ isovalent pair. All of these clusters are (3D) “aromatic”, characterized by multicenter bonding and alternating charges.

The aromatic properties, expressed through the NICS(0) values show an oscillatory odd−even behavior, with respect to the number of silicon (or boron) atoms. Although the NICS(0) value of $Si_4C_2H_2$ is nearly half the value of the corresponding carborane, the NICS(0) value of $Si_2C_4H_4$ is slightly larger than the $C_4B_2H_6$ value. Both of these effects could be related to the formation of Si/C ring subunits.

The IR and Raman spectra of the hydrogenated silicon−carbon clusters show characteristic lines around 3100 cm^{-1}, which for IR have low intensities (a few percent of the peak intensity) but for Raman exhibit the peak value.

The BH−Si replacement rule seems to work well not only for the $Si_nC_2H_2$−$C_2B_nH_{n+2}$ pairs but also for $Si_2C_4H_4$−$C_4B_2H_6$. Furthermore, from the top row of Figure 1, comparing structure 3 on the left for SiC_2H_2 with structure 2 on the right for C_2BH_2, we can see that the replacement of BH_2 with SiH, surprisingly enough, seems to work as well, at least for this particular case. Yet to generalize such a claim to other cases seems to be a bit shaky. It is anticipated, however, that for any B−H-bond-bearing compound the replacement of B−H by Si would lead to a low-energy local (or global) minimum Si-containing “homologous” structure. This should be particularly true for carborane compounds.

It is hoped that using this BH replacement ansatz and the well-known carborane and metallacarborane properties and capabilities for complex applications (cage, multicage, multidecker metallacarboranes sandwich complexes, etc.[16]), one should be able to design (and test) novel silicon carbon complex materials and metamaterials. The present work aims to serve as a fundamental contribution toward this direction.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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