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Aromaticity and antiaromaticity in the cyclic 6π and 4π molecules of carbon and silicon E_6H_6 and E_4H_4 (E = C, Si)

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Quantum chemical calculations using density functional theory at the BP86/def2-TZVPP level are reported for the structures and aromaticities of the monocyclic molecules E_6H_6 and E_4H_4 (E = C, Si). The results reveal drastic differences between the carbon and silicon homologues. Benzene (**1b**) is the global energy minimum on the C_6H_6 PES whereas planar D_{6h} Si_6H_6 (**2d**) is not an energy minimum and the D_{3d} form **2c** is higher in energy than the prismane isomer **2a**. There is an ubiquitous number of stable phenyl compounds but the only experimentally known Si_6R_6 compound has the structure of the tricyclic species **2b**, which is lower in energy than **2c**. In sharp contrast, the homologous carbon isomer **1c** is more than 120 kcal mol^{-1} higher in energy than **1b**. The carbon compounds C_6H_6 and C_4H_4 show a characteristic preference for substitution reaction of benzene **1b** and for addition reaction of cyclobutadiene **3a**. The Si_6H_6 silicon homologue **2c** has a weaker preference for substitution reaction than benzene, but also tetrasilacyclobutadiene **4a** prefers substitution over the addition reaction. The comparison of the calculated (pseudo) π conjugation of the cyclic compounds and acyclic reference systems suggests aromatic stabilization/destabilization for the carbon systems. The values for the silicon compounds are inconclusive and the separation of σ and π interactions is difficult due to the strong deviation of some silicon systems from planarity. The NICS values are not a reliable indicator for aromatic stabilization due to π conjugation. Chemical bonding models that have been developed and derived for compounds in the first octal series of the periodic table are only suitable to a limited extent for molecules with heavier main group atoms. This comes from the radii of the s/p valence orbitals of the atoms, which are very similar for the first octal row atoms leading to effective sp hybridization. The chemical bonds of the heavier atoms have a much higher p character because the radius is bigger than the valence s orbitals.

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Introduction

Aromaticity is a basic concept in chemistry that is frequently used to explain the structures, properties and chemical reactivity of a wide variety of compounds.[1,2] Despite the ubiquitous use of the term 'aromaticity', there is still much controversy as to whether molecules really possess genuine aromatic character. This is due to the fact that various properties are identified as characteristic features of aromatic compounds, which are often used only superficially and without critical examination of the proposed criteria.[3]

The term aromaticity was originally introduced to the field to account for the peculiar high stability and low reactivity of benzene and related molecules.[4,5] Benzene was isolated by Faraday in 1825.[6] The term "aromatic", which refers to the particular smell of the compounds, was used for the first time by Hofmann in 1855.[7] In 1865, Kekulé suggested a cyclic structure of benzene.[8] The preference of aromatic compounds for electrophilic substitution rather than addition reactions was reported by Erlenmeyer in 1866.[9] This is the primary property of aromatic compounds, which puzzled chemists for a long time. Unsaturated compounds usually undergo addition reactions with saturated species as products, but this particular class of cyclic unsaturated compounds resists addition reactions and rather engages in substitution reactions in which the unsaturated character is retained. A theoretical explanation for the particular chemical stability of benzene and related compounds was provided by Hückel in 1931 in terms of molecular orbital (MO) theory.[10] He showed that

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aromaticity in conjugated molecules can be associated with a specific number of delocalized π electrons, which was later expressed by Doering with the familiar formula $4n + 2$ that is usually called Hückel rule.[11]

In the course of time, a variety of other properties such as molecular structure (bond equalization), magnetic and spectroscopic features has been associated with the phenomenon of aromaticity and the field of compounds that were suggested to possess aromatic properties widely increased until today.[12] In particular, magnetic properties are nowadays often taken as evidence for aromaticity without the particular chemical behaviour of aromatic molecules, which is the resistance toward addition reactions, being investigated. Many aromaticity definitions in terms of magnetic properties have been proposed in the meantime,[13] the currently most prominent and widely used version being the NICS (Nuclear Independent Chemical Shift) method of Schleyer *et al.*[14] However, it must be recognised that structural and magnetic properties are secondary effects that may or may not correlate with the primary and original criterion for aromaticity, namely energetic stabilisation/destabilisation following the $4n + 2$ rule. We believe that much of the confusion and controversy surrounding the occurrence of aromaticity in compounds is due to the investigation of such secondary effects without taking into account the energetic stabilisation due to delocalisation of $4n + 2$ electrons. The focus of many studies lies on secondary properties, because they are much easier to calculate than the energetic stabilization due to aromaticity. This confuses much of the conclusion whether a new molecule is aromatic. This holds particularly for NICS values, which are easy to calculate.

Pascal discovered already in 1910 that aromatic compounds exhibit an unusually high diamagnetic susceptibility compared with nonaromatic reference systems.[15] This was explained with the induced ring current in cyclic delocalized molecules by Pauling,[16] by London[17] and by Lonsdale,[18] who had also shown in 1929 for the first time by X-ray crystallography that benzene has a planar hexagonal geometry.[19] The special magnetic behaviour that is associated with induced ring currents seemed to be closely related to the cyclic electron delocalization in aromatic compounds. But it is known by now that, although aromatic compounds like benzene exhibit strong diamagnetic susceptibility exaltation, the appearance of such ring currents can also be found in species that are chemically unstable and may energetically be unfavourable with respect to geometric distortion. For example, one of us reported in 2017 that the cyclic 10π electron systems $N_6H_6^{2+}$ (D_{6h}) and $C_2N_4H_6$ (D_{2h}), which are formally Hückel aromatic compounds that possess NICS values similar to benzene, are not only unstable towards nonplanar distortion but they are also much higher in energy than acyclic isomers.[20] This contradicts the suggested definition proposed by Schleyer for aromatic species: "compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization." If aromaticity is defined solely by magnetic properties, it loses its characteristic signature of chemical stability and the structural feature of a particular class of unsaturated compounds.

Although it has been shown that the magnetic properties and especially the NICS values are not reliable indicators for the particular stabilization of cyclic $4n + 2$ systems, they are routinely used as evidence for the observation of new aromatic compounds. This is especially true for cyclic silicon compounds as closest homologs of carbon compounds. In recent years, there have been several reports of silicon compounds that formally obey the $4n + 2$ rule for π-electrons and have been claimed to be examples of aromatic silicon compounds because they have NICS values indicative of aromatic stabilization.[38,40] This prompted us to analyse the electronic structure and energies of carbon and silicon compounds that are classic examples of aromatic and antiaromatic species.

The focus of this work lies on the aromatic/antiaromatic character of the cyclic 6π and 4π molecules of carbon and silicon E_6H_6 and E_4H_4 (E = C, Si). We compare the equilibrium structures of carbon and silicon and the propensity of the molecules for substitution and addition reactions. We also analyse the magnetic properties and conjugative stabilization with a variety of methods. The topic of this work concerns the question of whether the model of aromaticity/antiaromaticity, which is very useful and valid for carbon compounds, is also relevant for silicon compounds.

Methods

Geometry optimizations were performed by using Gaussian 16[21] at the BP86/def2-TZVPP[22] level of theory. Vibrational frequencies were calculated to find the number of imaginary modes *i*. In addition to DFT calculations, geometry optimizations and vibrational frequencies were also carried out at the RI[23]-MP2[24]/cc-pVTZ[25] level using the ORCA 6.0 program.[26] The NICS calculations were carried out using the BP86/def2-TZVPP optimized geometries using the gauge invariant atomic orbital (GIAO) method[27] at the B3LYP[28]/def2-TZVPP level. The strength of the conjugative stabilization was estimated with the EDA-NOCV method[29] at the ZORA[30]-BP86/TZ2P[31] level utilizing the ADF 2023 package[32] and the BP86/def2-TZVPP optimized geometries. Details about the method are available from recent review articles.[33]

Geometries and energies

Fig. 1 shows the optimized geometries and relative energies of E_6H_6 and E_4H_4 isomers, which are relevant for this study, at the BP86/def2-TZVPP and RI-MP2/cc-pVTZ levels of theory. The results are in good agreement with each other and with earlier studies.[34–37] The calculated structures may therefore be used for the analysis of the bonding situation. Benzene (D_{6h}) **1b** is the global energy minimum structure on the C_6H_6 potential energy surface (PES). In contrast, the planar D_{6h} form of Si_6H_6 **2d** is not an energy minimum structure, but a transition state (number of imaginary frequencies $i = 1$). Release of the D_{6h} symmetry constraint leads to the non-planar structure **2c** with a

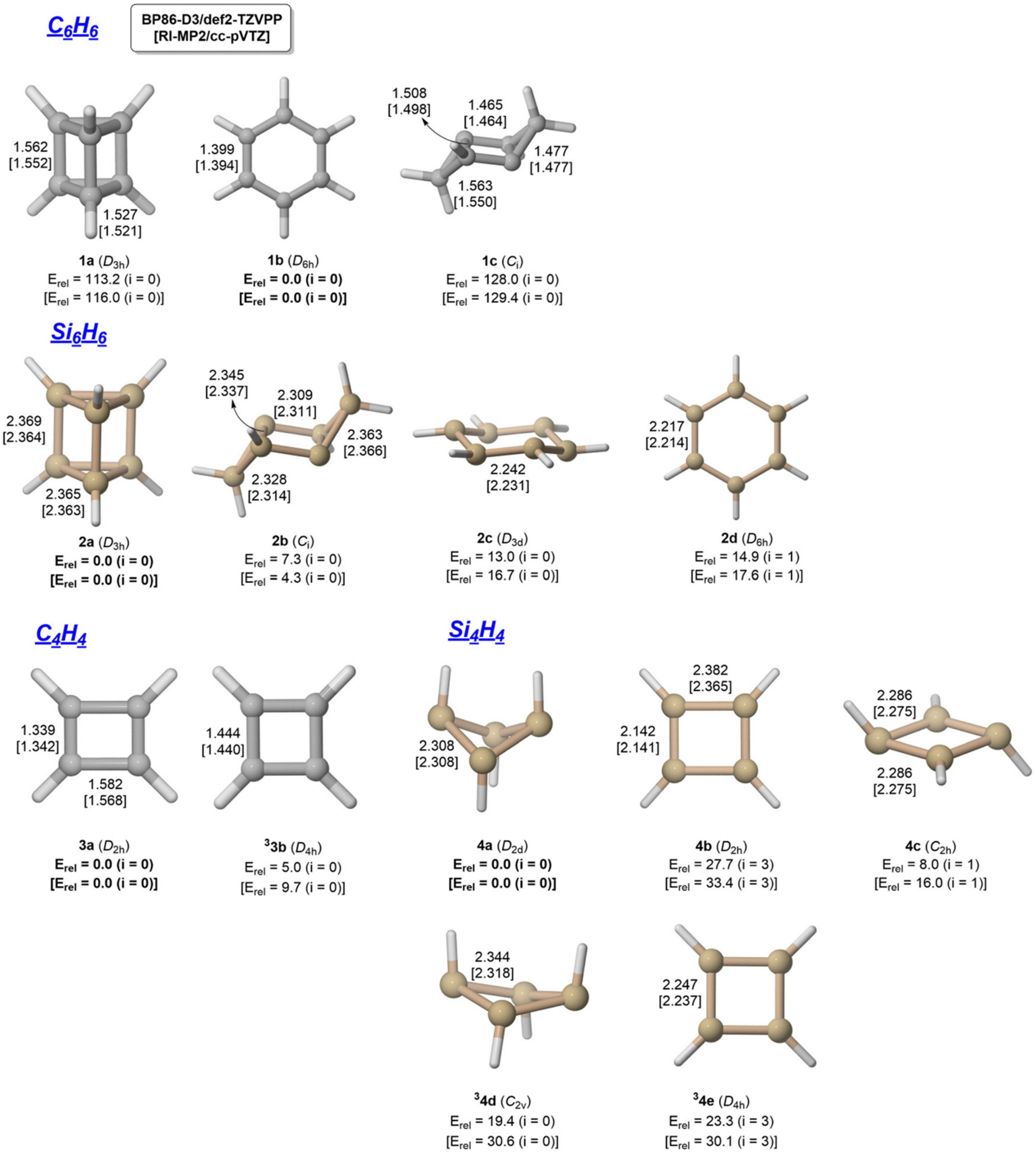


Fig. 1 Calculated geometries and relative energies of E_6H_6 and E_4H_4 isomers at BP86-D3/def2-TZVPP [RI-MP2/cc-pVTZ]. Bond lengths are given in Å, energies in kcal mol^{-1}. The number of imaginary modes (*i*) is also given.

chair conformation (D_{3d}), which is slightly lower in energy than **2d**. But the global energy minimum structure on the Si_6H_6 PES is the pyramidal isomer **2a**, which is clearly lower in energy than **2c**. This result has been reported before.[36] In contrast, the pyramidal form of carbon **1a** is a very high-lying isomer on the C_6H_6 PES.

The distortion and energy lowering of Si_6H_6 from the planar D_{6h} form **2d** to the non-planar D_{3d} structure **2c** can easily be explained when the chemical bonds of the heavier main-group atoms are considered and compared with those of the first octal-row atoms. The 2p electrons of the latter atoms do not face energetically lower-lying p electrons and therefore, they can penetrate rather deeply into the core. In contrast, the 2s electrons encounter 1s core electrons. This leads to a very similar radius of the 2s and 2p valence orbitals of the first octal-row atoms and yields an effective 2s/2p hybridization for covalent bonding which results from the interference of the wave functions. But the 3p valence electrons of the heavier atom Si face the 2p electrons and the radius of 3p AOs of Si is clearly bigger than that of the 3s AO. This means that covalent bonds of Si and heavier main-group atoms have a much higher (*n*)p character than those of carbon and other first octal-row atoms. The consequences become evident by the D_{3d} equilibrium geometry of Si_6H_6 whereas the planar D_{6h} form is a transition state. The NBO calculations show that the percentage p character of the Si–Si bonds in D_{3d} Si_6H_6 is higher ($sp^{2.1}$) than in D_{6h} Si_6H_6 ($sp^{1.9}$). But the energy lowering of D_{3d} Si_6H_6 comes from the change in the hybridization of the formally unbound electrons at Si which are in sp^x hybridized orbitals whereas they are in energetically higher lying pure 3p orbitals in D_{6h} Si_6H_6.

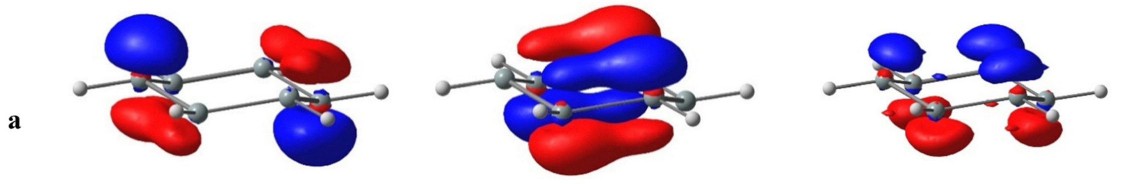
But there is another unusual isomer of C_6H_6 and Si_6H_6 which is very important for the present study. The only experimental study where a Si_6R_6 could be isolated is a compound with R = Tip (2,4,6-triisopropylphenyl) where the Si_6 moiety is actually a tricyclic isomer of hexasilabenzene, which exhibits the structural feature of isomer **2b**.[38] The latter Si_6H_6 species is lower in energy than the chair conformational minimum **2c** but still higher in energy than hexasilaprismane **2a**. Examination of the Si–Si bonds in **2b** shows that this isomer should be considered as a substituted cyclic $Si_4H_2R'_2$ species where R′ is a bridging SiH_2 moiety. Silicon prefers a cyclic Si_4R_4 moiety over Si_6R_6, which is opposite to the behaviour of carbon compounds. We calculated the related tricyclic C_6H_6 isomer **1c**, which is an energy minimum but >125 kcal mol^{-1} higher lying than benzene (Fig. 1). The unusual isomer **1c** was missed in the systematic study of C_6H_6 where 209 isomers were identified.[34] Chemical knowledge derived from compounds of the first octal row atoms of the periodic system is not very helpful to understand the structures and bonding situation of heavier main-group compounds. This was actually shown already some decades ago by Kutzelnigg.[39]

The calculated structures of E_4H_4 exhibit similarly drastic differences between C and Si as the E_6H_6 species. The global energy minimum structure of cyclobutadiene C_4H_4 is the rectangular species **3a** (D_{2h}) in the electronic singlet state with two short and two long C–C bonds. The square planar isomer in the electronic triplet state ^{3}**3b** (D_{4h}) is slightly higher in energy, which agrees with earlier high-level *ab initio* calculations.[37] Unlike the carbon homologue, the planar rectangular structure of Si_4H_4 **4b** in the electronic singlet state has three imaginary frequencies (i = 3). Geometry optimization without symmetry constraints leads to the significantly more stable nonplanar structure **4a** (D_{2d}), which is the global energy minimum on the Si_4H_4 PES. The square-planar triplet species ^{3}**4e** (D_{4h}) has like the singlet structure **4b** three imaginary frequencies (i = 3). Unconstrained geometry optimization leads to the nonplanar structure ^{3}**4d** (D_{2d}), which is less puckered than the singlet isomer **4a** (D_{2d}), but it is much higher in energy. But there is one more structure on the Si_4H_4 PES, which is not much higher in energy than **4a** but has a planar Si_4 ring. Geometry optimization of the singlet species with the constraint of a planar Si_4 ring leads to **4c**, which has a square-planar Si moiety where two hydrogens in the 1,3 position are in the plane whereas two hydrogens in the 2,4 position are bent away in *anti* position of the ring. Structure **4c** has one imaginary frequency which points towards distortion of the planar ring in the direction of **4a**. However, several substituted tetrasilabutadienes Si_4R_4 could be isolated and structurally characterized by X-ray crystallography.[40] The common feature of all these compounds is an almost planar or slightly folded Si_4 ring with four not very different Si–Si distances with rhombic distortion, which is likely due to substituent effects.

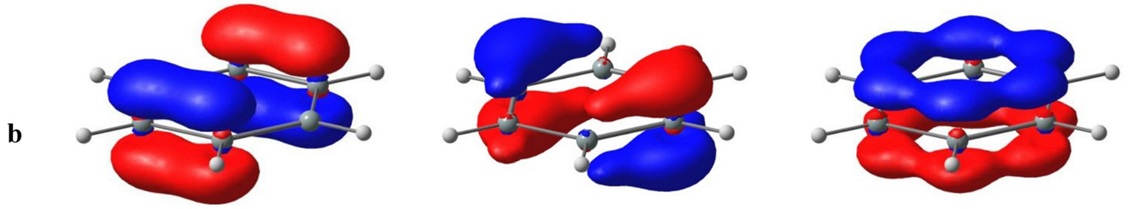
How does the different symmetry of the silicon species affect the electronic structure of the molecules with regard to the π aromaticity? Fig. 2b and d show the occupied valence π orbitals of planar Si_6H_6 **2d** (D_{6h}) and planar Si_4H_4 **4b** (D_{2h}), which exhibit the well-known pattern of C_6H_6 and C_4H_4 in the electronic singlet state. Fig. 2a and c show the energetically highest lying occupied orbitals of the energy minimum structures of Si_6H_6 **2c** (D_{3d}) and Si_4H_4 **4a** (D_{2d}). The degenerate HOMO and the HOMO−1 of Si_6H_6 **2c** (D_{3d}) still possess a similar shape as the related π MOs of planar Si_6H_6 **2d** (D_{6h}). In contrast, the shape of the energetically highest-lying orbitals HOMO and HOMO−1 of puckered Si_4H_4 **4a** (D_{2d}) does not resemble the energetically highest-lying π MOs of planar Si_4H_4 **4b** (D_{2h}). This is not surprising, because the Si–H bonds take an axial position in Si_4H_4 **4a** (D_{2d}) whereas they are in an equatorial position in Si_6H_6 **2c** (D_{3d}). The HOMO and HOMO−1 of Si_4H_4 **4a** (D_{2d}) have lone-pair character extended to all four silicon atoms. It is noteworthy that the HOMO and HOMO−1 of Si_4H_4 **4a** (D_{2d}) are much lower in energy than those of planar Si_4H_4 **4b** (D_{2h}). The deviation from planarity strongly enhances the stability of the valence electrons in Si_4H_4 **4a** (D_{2d}). There is also a change in the symmetry of the orbitals. The HOMO of Si_4H_4 **4a** (D_{2d}) is (weakly) bonding over all four Si atoms like the HOMO−1 of planar Si_4H_4 **4b** (D_{2h}). In contrast, the HOMO−1 of Si_4H_4 **4a** (D_{2d}) has two nodes and there is 1,3 and 2,4 trans-annular attraction, while the HOMO of planar Si_4H_4 **4b** (D_{2h}) has only one node and 1,2 and 3,4 π bonding character.

We calculated the reaction energies of E_6H_6 **1b** (E = C), **2c** (E = Si) and E_4H_4 **3a** (E = C), **4a** (E = Si) for 1,2 addition and 1,2 hydrogen substitution with Cl_2. The results are shown in Table 1. The results for the substitution reactions are given for the formation of the most stable conformations where the chlorine atoms are at the *trans*(eq,eq) position. The reaction energies for benzene **1b** agree with the well-known tendency of aromatic compounds. The substitution reaction 2 is exergonic by −52.1 kcal mol^{-1} whereas the addition reaction 1 is endergonic by 6.3 kcal mol^{-1}. There is an energy difference of Δ = 58.4 kcal mol^{-1} in favor of the substitution reaction. A much smaller gap between the two reactions is predicted for Si_6H_6 **2c**. The substitution reaction 4 of the Si compound is even more exergonic (−114.2. kcal mol^{-1}) than for benzene **1b**, but the addition reaction 3 is also exergonic by −85.0 kcal mol^{-1}. This gives an energy difference of Δ = 29.2 kcal mol^{-1} in favor of the substitution reaction of the Si species.

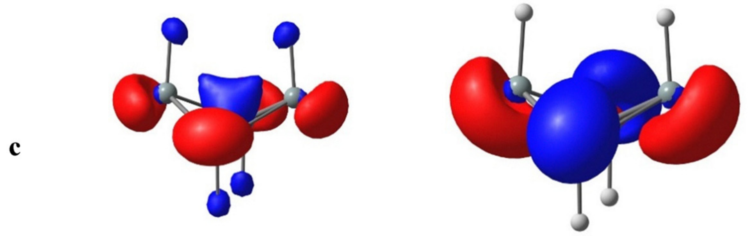
A qualitatively different result of the substitution and addition reactions is found between the C_4H_4 species **3a** and Si_4H_4 **4a**. Table 1 shows that the addition reaction 5 of C_4H_4 (**3a**) is, as expected, energetically favored (ΔG = −67.8 kcal mol^{-1}) over the substitution reaction 6 (ΔG = −58.2 kcal mol^{-1}) which underlines the reaction energies as a criterion for the antiaromaticity of 4π systems. The addition reaction 6 of the C_4H_4 species **3a** is favored by Δ = 9.6 kcal mol^{-1}. However, such a reversal of the reaction energies for substitution and addition reactions is not found for Si_4H_4 **4a**. Table 1 shows that the addition reaction 7 of Si_4H_4 (**4a**) is energetically disfavored (ΔG = −101.0 kcal mol^{-1}) over the substitution reaction 8 (ΔG = −113.3 kcal mol^{-1}) which



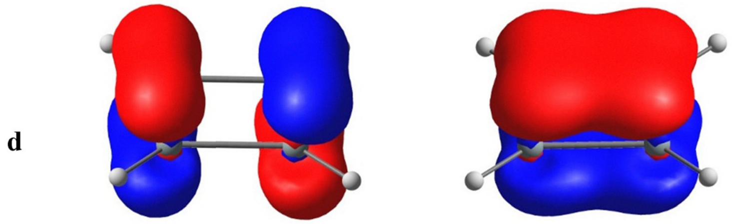
2c (HOMO, -5.45 eV, E_g) **2c** (HOMO, -5.45 eV, E_g) **2c** (HOMO-1, -6.59 eV, A_{2u})



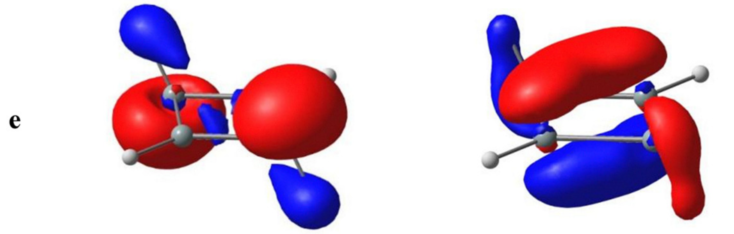
2d (HOMO, -5.28 eV, E_{1g}) **2d** (HOMO, -5.28 eV, E_{1g}) **2d** (HOMO-1, -6.41 eV, A_{2u})



4a (HOMO, -5.86 eV, A1) **4a** (HOMO-1, -6.31 eV, B2)



4b (HOMO, -0.15 eV, B1) **4b** (HOMO-1, -0.23 eV, B1)



4c (HOMO, -5.30 eV, A_g) **4c** (HOMO-1, -6.15 eV, A_u)

Fig. 2 Plot of the energetically highest lying occupied MOs of **2c**, **2d**, **4a**, **4b**, **4c** (isosurface value of 0.04 a.u., a–e). All data have been computed at the BP86/def2-TZVPP level.

contradicts the reaction energies as a criterion for the antiaromaticity of 4π systems of silicon. The substitution reaction 8 of the Si_4H_4 species **4a** is favored by $\Delta = 12.3$ kcal mol^{-1} over the addition reaction 7. Note that the substitution reaction of Si_4H_4 (**4a**) has nearly the same reaction energy ($\Delta G = -113.3$ kcal mol^{-1}) as that of Si_6H_6 (**2c**) ($\Delta G = -114.2$ kcal mol^{-1}). The addition reaction of Si_4H_4 (**4a**) is higher ($\Delta G = -101.0$ kcal mol^{-1}) than that of Si_6H_6 (**2c**) ($\Delta G = -85.0$ kcal mol^{-1}) but the increase is not large enough to surpass the value of the substitution reaction as in the case of the carbon species. Therefore, the calculated reaction energies do

Table 1 Calculated reaction energies (kcal mol^{-1}) of substitution and addition reactions of E_6H_6 and E_4H_4 (E = C, Si). All data were computed at the BP86/def2-TZVPP level

	Reaction	ΔE (ΔG)	Δ
1	C_6H_6 (**1b**) + Cl_2 → $C_6H_6Cl_2$	−2.4 (+6.3)	
2	C_6H_6 (**1b**) + $2Cl_2$ → $C_6H_4Cl_2$ + 2HCl	−52.7 (−52.1)	−50.3 (−58.4)
3	Si_6H_6 (**2c**) + Cl_2 → $Si_6H_6Cl_2$	−93.2 (−85.0)	
4	Si_6H_6 (**2c**) + $2Cl_2$ → $Si_6H_4Cl_2$ + 2HCl	−114.5 (−114.2)	−21.3 (−29.2)
5	C_4H_4 (**3a**) + Cl_2 → $C_4H_4Cl_2$	−78.0 (−67.8)	
6	C_4H_4 (**3a**) + $2Cl_2$ → $C_4H_2Cl_2$ + 2HCl	−59.7 (−58.2)	+18.3 (+9.6)
7	Si_4H_4 (**4b**) + Cl_2 → $Si_4H_4Cl_2$	−110.0 (−101.0)	
8	Si_4H_4 (**4b**) + $2Cl_2$ → $Si_4H_2Cl_2$ + 2HCl	−113.6 (−113.3)	−3.6 (−12.3)

not suggest that (pseudo) 4π systems of silicon exhibit any particular instability due to antiaromaticity.

Conjugation and NICS values

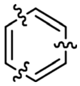
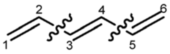
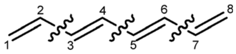
We calculated the magnetic currents given by the NICS method and the strength of the (pseudo) π conjugation in the carbon and silicon systems E_6H_6 and E_4H_4. The (pseudo) π conjugation was estimated using the EDA-NOCV method, in which the molecules are broken down into appropriately selected fragments, their interactions are calculated and where the energy terms $\Delta E_{\mathrm{elstat}}$, $\Delta E_{\mathrm{Pauli}}$, ΔE_{orb} provide a series of physically meaningful terms that allow a quantitative estimate of the interacting forces between the fragments. The genuine π conjugation is directly available from the orbital term ΔE_{orb} for molecules that have a mirror plane. This has been proven as a useful method to investigate the strength of conjugation, hyperconjugation and aromaticity in a variety of molecules.[2d,41] For non-planar molecules it is possible to estimate the pseudo-π conjugation by examination of the pairwise orbital interactions, which is given by the NOCV calculations. The fragments do not share a common mirror plane, but the interfragment interactions exhibit two orbital terms, which are the large electron-sharing (pseudo) σ bond formation and the weaker (pseudo) π conjugation. The shape of the associated fragment orbitals and the connected density deformation allow us to clearly distinguish the two types of orbital interactions.

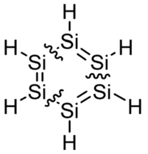
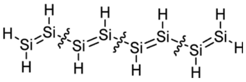
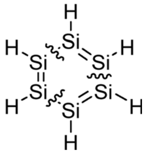
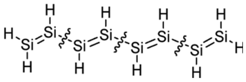
The results for E_6H_6 are shown in Table 2. The data for benzene clearly supports the model of additional aromatic π conjugation in the cyclic molecules. The calculated π conjugation in C_6H_6 between three C_2H_2 fragments is −107.5 kcal mol^{-1}, which is much higher than the π conjugation between fragments in acyclic C_6H_8 (−41.5 kcal mol^{-1}). The difference gives a value of 66.2 kcal mol^{-1} for the aromatic stabilization energy (ASE). However the π conjugation in acyclic C_6H_8 comes from only two conjugating bonds, whereas there are three conjugating bonds in benzene C_6H_6. A more appropriate acyclic reference system with three conjugating units is C_8H_{10}, which gives a slightly smaller ASE of 42.0 kcal mol^{-1}. We shall use the latter ASE value as a reference number for the stabilization due to aromatic conjugation. The NICS values for benzene shown in Table 2 agree with earlier studies using different DFT functionals. They are also used as reference values for aromaticity. As noted in the introduction, although the 10π planar molecule $N_6H_6^{2+}$ (D_{6h}) NICS values of NICS(0) = −17.6 ppm, (NICS(1) = −8.3 ppm), NICS(1)$_{zz}$ = −25.7 ppm and $C_2N_4H_6$ (D_{2h}), NICS(0) = −15.5 ppm, (NICS(1) = −7.5 ppm), NICS(1)$_{zz}$ = −25.5 ppm, resemble those of C_6H_6, the cyclic molecules are much higher in energy than acyclic isomers.[20]

The results for the silicon systems are given in the lower columns of Table 2. Planar Si_6H_6 (D_{6h}) possesses similar NICS values as benzene, whereas the conjugative stabilization with regard to acyclic planar Si_8H_{10} (C_{2h}) gives a much smaller ASE value of 19.9 kcal mol^{-1} compared with benzene. But these are fictitious numbers that come from non-equilibrium structures. More relevant are the calculated values for the (pseudo) π conjugation in the energy minima of Si_6H_6 (D_{3d}) and Si_8H_{10} (C_i). The computed ASE of 14.3 kcal mol^{-1} suggests a weaker but still substantial stabilization due to (pseudo) π conjugation. The NICS values indicate a magnetic susceptibility for Si_6H_6 (D_{3d}), which has a similar magnitude as in benzene. But neither the strength of the (pseudo) π conjugation nor the NICS values correlate with the energetic stabilization of **2c** and **2d** relative to **2b** and **2a**, which are lower in energy. This is opposite to the carbon system C_6H_6, where the related isomers **1a** and **1c** are >100 kcal mol^{-1} higher in energy than benzene **1b**. But the main finding of the data shown in Table 2 is that, although Si_6H_6 (D_{6h}) encounters aromatic stabilization of 19.9 kcal mol^{-1}, it is not even an energy minimum on the PES and that several structural isomers are lower in energy. There are obviously other factors than 4n + 2 π delocalization, which determine the stability of the molecule. This is different from the carbon homologue.

The results for the cyclic E_4H_4 species and the acyclic reference compounds are shown in Table 3. The negative ASE value for cyclobutadiene **3a** (−32.0 kcal mol^{-1}) is indicative of a strongly antiaromatic character. The positive NICS values agree with the assignment of antiaromaticity of **3b**. Both indicators nicely correlate with the preference of cyclobutadiene for addition reaction rather than substitution (Table 1). Similar results are obtained when the homologous planar Si_4H_4 species **4b** and the acyclic planar reference system Si_6H_8 (C_{2h}) are compared. There is a negative ASE value of −19.0 kcal mol^{-1} and positive NICS values for **4b**. But the carbon compounds are energy

Table 2 Calculated EDA-NOCV results (ZORA-BP86/TZ2P//BP86/def2-TZVPP level) for cyclic E_6H_6 (E = C, Si) and for acyclic reference systems, which show (in bold text) the strength of the (pseudo) π conjugation and the aromatic stabilization energies ASE in kcal mol^{-1}. Calculated NICS values (GIAO-B3LYP/def2-TZVPP//BP86/def2-TZVPP level) in ppm

Molecule			
Symmetry	D_{6h} (**1b**)	C_{2h}	C_{2h}
ΔE_{int}	−513.3	−308.7	−489.6
ΔE_{Pauli}	1174.2	688.9	1060.7
ΔE_{elstat}	−537.7	−340.2	−510.5
ΔE_{Orb}	−1149.7	−657.3	−1039.8
ΔE_{σ}	−1042.2	−615.8	−974.3
ΔE_{π}	**−107.5**	**−41.5**	**−65.5**
$r(E-E)$/Å	1.399		
Fragments	$3C_2H_2$ (os)	$2C_2H_3$(d) + C_2H_2(os)	$2C_2H_3$(d) + $2C_2H_2$(os)
ASE	**66.2**		
	42.0		
NICS(0)	−8.3		
NICS(1)	−9.9		
NICS(1)$_{zz}$	−29.7		

Molecule				
Symmetry	D_{6h} (i = 1) (**2d**)	C_{2h} (i = 4)	D_{3d} (i = 0) (**2c**)	C_i (i = 0)
ΔE_{int}	−287.7	−289.0	−247.9	−282.8
ΔE_{Pauli}	511.5	471.4	561.4	503.4
ΔE_{elstat}	−272.8	−271.4	−319.6	−293.5
ΔE_{Orb}	−526.4	−489.0	−489.7	−492.7
ΔE_{σ}	−463.7	−446.1	−433.9	−453.4
ΔE_{π}	**−62.7**	**−42.8**	**−49.5**	**−35.2**
$r(E-E)$/Å	2.217		2.242	
Fragments	$3Si_2H_2$(os)	$2Si_2H_3$(d) + $2Si_2H_2$(os)	$3Si_2H_2$(os)	$2Si_2H_3$(d) + $2Si_2H_2$(os)
ASE	**19.9**		**14.3**	
NICS(0)	−12.9		−10.6	
NICS(1)	−11.9		−9.5	
NICS(1)$_{zz}$	−20.0		−18.6	

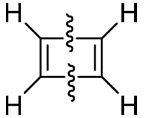
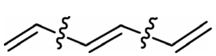
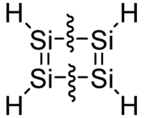
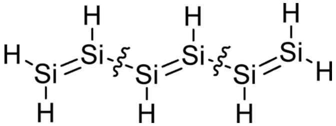
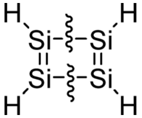
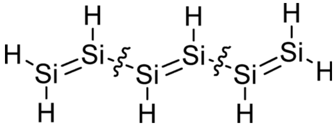
minima whereas the silicon species have three imaginary frequencies. More relevant are the calculated results for **4c** and the acyclic energy minimum Si_6H_8 (C_i), which give a small positive ASE value of 2.8 kcal mol^{-1} and negative NICS data except for the NICS(1)$_{zz}$ value. EDA-NOCV calculations of **4a** did not provide meaningful data, because σ and (pseudo) π interactions cannot be distinguished due to the strongly puckered Si_4 ring. But the comparison of the ASE and NICS values of C_4H_4 (**3a**) with Si_4H_4 (**4c**) clearly shows significant differences between the carbon and the silicon homologues.

Discussion

The calculated structures and reaction energies toward addition and substitution reactions of the cyclic E_6H_6 and E_4H_4 species and the bonding analysis using the EDA-NOCV method and the NICS approach reveal substantial differences between the carbon and the silicon compounds. Benzene is the global energy minimum on the C_6H_6 PES and there is an infinite number of stable phenyl derivatives. In contrast, planar D_{6h} Si_6H_6 (**2d**) is not an energy minimum and the D_{3d} form **2c** is higher in energy than the prismane isomer **2a**, which is the global energy minimum on the Si_6H_6 PES. There is no experimental evidence for a Si_6H_6 species and the only known derivative with the formula Si_6R_6 is a tricyclic species. The parent tricyclic isomer Si_6H_6 **2b** is even lower in energy than **2c**, whereas the analogous carbon isomer **1c** is more than 120 kcal mol^{-1} less stable than benzene. Similar differences are found for the E_4H_4 species. The global energy minimum of butadiene is the planar structure **3a** whereas the most stable structure of Si_4H_4 is the strongly puckered form **4a**.

Similar grave differences are found for the calculated reaction energies of E_6H_6 and E_4H_4 for addition and substitution reactions, which are relevant for the assignment of aromatic stability. The carbon compounds show a characteristic preference for the substitution reaction of benzene **1b** and for the addition reaction of cyclobutadiene **3a**. The Si_6H_6 silicon homologue **2c** has a weaker preference for substitution reaction than benzene, but also tetrasilacyclobutadiene **4a** prefers substitution to the addition reaction. The calculated ASE values, which are obtained from EDA-NOCV calculations of the cyclic

Table 3 Calculated EDA-NOCV results (ZORA-BP86/TZ2P//BP86/def2-TZVPP level) for cyclic E_4H_4 (E = C, Si) and for acyclic reference systems, which show (in bold text) the strength of the (pseudo) π conjugation and the aromatic stabilization energies ASE in kcal mol^{-1}. Calculated NICS values (GIAO-B3LYP/def2-TZVPP//BP86/def2-TZVPP level) in ppm

Molecule						
Symmetry	D_{2h} (i = 0) (**3a**)	C_{2h} (i = 0)	D_{2h} (i = 3) (**4b**)	C_{2h} (i = 3)	C_s (i = 1) (**4c**)	C_i (i = 0)
ΔE_{int}	−190.0	−278.9	−120.2	−169.3	−123.3	−162.1
ΔE_{Pauli}	360.0	499.2	194.41	227.9	310.2	276.5
ΔE_{elstat}	−218.3	−339.1	−133.8	−176.3	−192.8	−195.9
ΔE_{Orb}	−331.7	−439.1	−180.8	−221.0	−240.7	−242.8
ΔE_{σ}	−322.2	−397.4	−174.5	−193.7	−206.4	−207.9
$\boldsymbol{\Delta E_{\pi}}$	**−9.6**	**−41.6**	**−8.3**	**−27.3**	**−32.4**	**−29.6**
$r(E-E)$/Å	1.339/1.582		2.142/2.382		2.286/2.286	
Fragments	$2C_2H_2$(t)	$2Si_2H_3$(d) + Si_2H_2(t)	$2Si_2H_2$(t)	$2Si_2H_3$(d) + Si_2H_2(t)	$2Si_2H_2$(t)	$2Si_2H_3$(d) + Si_2H_2(t)
ASE	**−32.0**		**−19.0**		**2.8**	
NICS(0)	+27.1		+15.4		−4.3	
NICS(1)	+17.5		+28.0		−3.5	
NICS(1)$_{zz}$	+56.0		+98.1		+5.8	

species and acyclic reference systems correlate nicely with the reaction energies of the carbon compounds but not so for the silicon species. The π conjugative stabilization of Si_6H_6 (D_{6h}) is not sufficiently strong to ensure the structural stability of the molecule. There are other factors which are responsible for the equilibrium geometry. The NICS values of the silicon molecules do not agree with higher stability due to aromatic conjugation.

The drastic change of the structures, reactivities and bonding situation between carbon compounds and heavier group-14 atoms is not restricted to the aromaticity/antiaromaticity of E_6H_6 and E_4H_4 species, but it is a general observation for molecules of the first octal row of the periodic system and heavier main-group atoms. A pertinent example is the heavier homologues of acetylene. The global energy minimum of C_2H_2 is HC≡CH with a carbon–carbon triple bond where the only other isomer is vinylidene $H_2C{=}C$, which is an energetically high-lying shallow energy minimum. The heavier homologues E_2H_2 (E = Si, Ge, Sn, Pb) have completely different structures. The most stable structures are the doubly and singly bridged isomers **A** and **B** (Fig. 3), which have been observed in low-temperature matrices,[42] whereas the linear structure with a triple bond HE≡EH is a second-order saddle-point.[43] Substituted homologues E_2R_2 (E = Si, Ge, Sn, Pb) with bulky groups R possess the structures **D1** or **D2**, because of steric repulsion in the bridged structures **A** and **B**.[44] The difference between acetylene and the heavier homologues E_2H_2 (E = Si, Ge, Sn, Pb) has been explained with the electronic states of the EH species in the E_2H_2 molecules, which can be traced back to the radii of the s/p valence orbitals of the group-14 atoms.[43] The same reasoning explains why the most stable form of nitrogen is N_2 whereas the lowest energy form of phosphorous is P_4, although the π bonds in P_2 have a higher percentage contribution to the total orbital interaction than in N_2.[45] The bottom line is, that bonding models that were derived for molecules of atoms of the first octal row of the periodic system have limited value for compounds of heavier homologues. This comes mainly from the different radii of the s/p valence orbitals, which have similar values only for the first octal row atoms.

We would also like to point out that the Si–Si π itself is not weak, as one might assume based on our results. On the contrary, the stabilizing contribution of the two doubly π orbitals in singlet ($^1\Sigma_g^+$) Si_2 to the total orbital interaction is even stronger (62%) than the σ orbital (38%).[46] But the electronic ground state of Si_2 is the triplet ($^3\Sigma_g^-$) state, which has only singly occupied π orbitals and a longer bond (2.303 Å) than the singlet ($^1\Sigma_g^+$) state (2.071 Å). Shorter bonds are not always lower in energy than longer bonds! The crucial factor is not the absolute values of the π bonds but the energy difference between σ and π bonds. The bigger radius of the 3p orbitals than the 3s orbitals leads to stronger single bonds with higher p character at longer distances, whereas the similar radii of the 2s and 2p AOs leads to more effective s/p hybridization and to a competition of σ and π orbitals. This is the reason why molecules with genuine double and triple π bonds are ubiquitous for first octal-row atoms, while they are rare for heavier main-group atoms. Another important factor for the structure

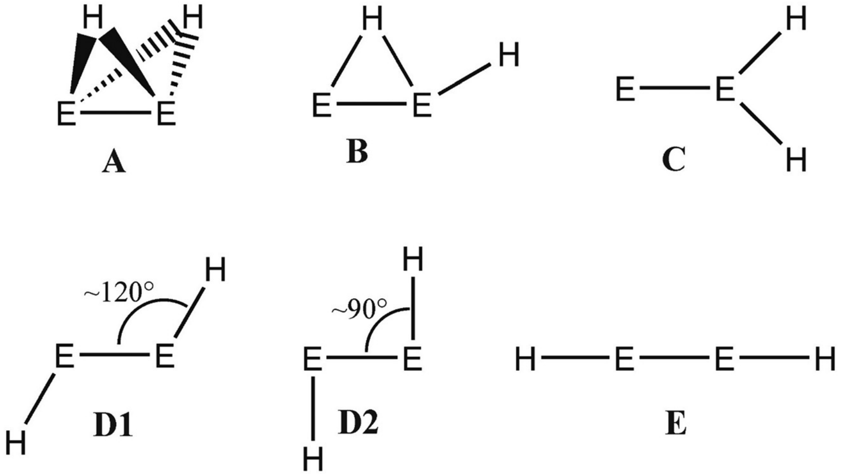


Fig. 3 Schematic representation of the energy minima of E_2H_2 (E = C–Pb). Only structures C and E are energy minima for E = C whereas A, B, C, D1, D2 but not E are energy minima for the heavier homologues E = Si–Pb.

and stability of molecules, which determines the equilibrium bond lengths of most compounds, is the Pauli repulsion between electrons having the same spin.[46]

Summary and conclusion

- Quantum chemical calculations of the structures and reactivities of the monocyclic molecules E_6H_6 and E_4H_4 (E = C, Si) reveal drastic differences between the carbon and silicon homologues. Benzene (**1b**) is the global energy minimum on the C_6H_6 PES whereas planar D_{6h} Si_6H_6 (**2d**) is not an energy minimum and the D_{3d} form **2c** is higher in energy than the prismane isomer **2a**. There is an ubiquitous number of stable phenyl compounds but the only experimentally known Si_6R_6 compound has the structure of the tricyclic species **2b**, which is lower in energy than **2c**. In sharp contrast, the homologous carbon isomer **1c** is more than 120 kcal mol^{-1} higher in energy than **1b**.
- The carbon compounds C_6H_6 and C_4H_4 show a characteristic preference for substitution reaction of benzene **1b** and for addition reaction of cyclobutadiene **3a**. The Si_6H_6 silicon homologue **2c** has a weaker preference for substitution reaction than benzene, but also tetrasilacyclobutadiene **4a** prefers substitution over the addition reaction.
- The comparison of the calculated (pseudo) π conjugation of the cyclic compounds and acyclic reference systems suggests aromatic stabilization/destabilization for the carbon systems. The values for the silicon compounds are inconclusive and the separation of σ and π interactions is difficult due to the strong deviation of some silicon systems from planarity.
- The NICS values are not reliable indicators for aromatic stabilization due to π conjugation. Aromatic compounds usually have characteristic NICS values, but the inverse correlation is not always given. The NICS values of the isolated, cyclic Si_4R_4 system are not reliable indicators of the factors that are decisive for the stability of the compound.
- Chemical bonding models that have been developed and derived for compounds in the first octal series of the periodic table are only suitable to a limited extent for molecules with heavier main group atoms. This holds particularly for aromatic stabilization following the $4n + 2$ rule, which appears to be valid only for compounds of the first octal row atoms. This comes from the radii of the s/p valence orbitals of the atoms, which are very similar for the first octal row atoms leading to effective sp hybridization. The chemical bonds of the heavier atoms have a much higher p character because the radius is bigger than the valence s orbitals.

Conflicts of interest

There are no conflicts to declare.

Data availability

All additional data are given as SI. Tables of the coordinates and energies of the calculated molecules. Details of the EDA-NOCV calculations. See DOI: **https://doi.org/10.1039/d5cp02697k**

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