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A Deeper Insight Into Strain For The Sila-Bi[6]Prismane ($\text{Si}_{18}\text{H}_{12}$) Cluster With Its Endohedrally Trapped Silicon Atom, $\text{Si}_{19}\text{H}_{12}$

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Abstract: A new family of over-coordinated hydrogenated silicon nanoclusters with outstanding optical and mechanical properties has recently been proposed. For one member of this family, namely the highly symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal, strain calculations have been presented with the goal to question its thermal stability and the underlying mechanism of ultrastability and electron-deficiency aromaticity. Here, the invalidity of these strain energy (SE) calculations is demonstrated mainly based on a fundamentally wrong usage of homodesmotic reactions, the miscounting of atomic bonds, and arithmetic errors. Since the article in question is entirely anchored on those erroneous SE values, all of its conclusions and predictions become without meaning. We provide evidence here that the nanocrystal in question suffers from such low levels of strain that its thermodynamical stability should be largely sufficient for device fabrication in a realistic plasma reactor. Most remarkably, the two "alternative," irregular isomers explicitly proposed in the aforementioned article are also electron-deficient, nontetrahedral, ultrastable, and aromatic nicely underlining the universality of the ultrastability concept for nanometric hydrogenated silicon clusters.

Introduction

The low-temperature plasma environment presents a powerful tool for the creation of nano-objects with unusual atomic structures and properties.¹ One example is the spontaneous formation of highly symmetric silicon hydride nanoclusters by self-assembly in a plasma reactor.²⁻⁹ While those nanocrystals are sufficiently stable for many possible applications,¹⁰ they are far away from global minimum energy structures. The transformation of metastable plasma-born silicon nanoclusters to extremely stable, over-coordinated, but irregular ones under the excessive influence of atomic hydrogen has been known for many years.² The origin for the astonishing stability of those clusters, namely electron delocalization induced by electron-deficient bonds, however, has only been understood recently.¹¹

The thermal stability of the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal has recently been questioned based on strain energy (SE) calculations.¹² Here, we unveil the fundamental errors that led the authors to their unfounded conclusions and predictions. Furthermore, we present evidence that the ring strain in $\text{Si}_{19}\text{H}_{12}$ does not jeopardize its stability for possible applications.

Computational Details

Most of the simulation details have been published elsewhere.⁸ ¹¹ Therefore, we just like to remind here that all *ab initio* molecular dynamics (AIMD) simulations were performed with the VASP program.^{13, 14} All optimizations were systematically accomplished at a B3LYP and MP2 level of theory with the 6-311++G(d,p) basis set yielding nearly identical results.¹⁵ The B3LYP functional was also used with the same basis set for time-dependent density functional theory (DFT) calculations for the absorption spectra. For the quantitative characterization of aromaticity, we have calculated magnetically induced aromatic ring currents.^{11, 16-20}

Results and Discussions

Scientific invalidity of recent SE calculations

SE calculations can be of precious help in understanding or predicting the relative stabilities and structural details of comparable molecules especially in the absence of experimental data or AIMD simulations. Although strain is not an experimental observable, schemes have been developed to estimate it quantitatively. To this end, one generally starts out from a "strain-free" reference structure and deforms it to the configuration in question. If this final structure and the initial one have exactly the same number and same nature of bonds, then the energy needed for the deformation will correspond to the SE. This simple concept is the basis for the homodesmotic reaction approach in estimating molecular strain energies, which was initially developed exclusively for hydrocarbon molecules.²¹ Despite the fact that there remains some doubt concerning its applicability to nonhydrocarbons,²² it presents the most often used method to estimate strain energies in all molecular systems. The most crucial condition for a successful SE calculation is the identification of a suitable "strain-free" reference compound.

The SE calculations presented in Ref. [[12]] for the symmetric Si₁₉H₁₂ nanocrystal are invalid for three important reasons:

1. Over time, many different definitions concerning the use of homodesmotic reactions have been developed. Nevertheless, they all demand equal numbers of each type of carbon-carbon bond ($C_{sp^3}-C_{sp^3}$, $C_{sp^2}-C_{sp^3}$, $C_{sp^2}-C_{sp^2}$, $C_{sp^2}=C_{sp^2}$ etc.) in reactants and products.²² The authors of Ref. [[12]] did not respect this fundamental rule. For the reactants, they used 24 highly electron-deficient bonds (6 bonds with an occupancy of only 1.64 electrons, 12 bonds with 1.84 electrons, and 6 formal half bonds with 1.05 electrons^[8]) while all bonds of the products correspond to fully occupied two electron single bonds; in addition, the reactants contain a mixture of sp^3-sp^3 , sp^2-sp^2 , sp^2-sp^1 , sp^2-sp^3 , etc. bonds while their products are purely sp^3 -hybridized. Consequently, this way of using homodesmotic reactions is as wrong as having an unbalanced number of single and double bonds for the reactants and the products; or in other words: the authors were not able to present any valid reference molecule to base their strain calculation on.
2. Yet more importantly: the number of silicon-silicon bonds has to be identical for the reactants and the products.^{21, 22} In Ref. [[12]], however, there are 68 Si-Si bonds for the reactants, but only 64 Si-Si bonds for the products. Consequently, the value given as an "upper bound" for the SE of the symmetric $Si_{19}H_{12}$ is nothing else, but a meaningless number.
3. For their "lower bound" SE estimate, the authors "invented" their own method unluckily without giving either any convincing explanations or references. However, admitting their method, the authors have used incorrect numbers: in their approach, the authors calculate the "single-point SE" [$SE(Si_{18}H_{12}-SP)$] for the nonoptimized $Si_{18}H_{12}$ cluster and evaluate it to be 11.78 eV. However, this value is higher than their SE for the optimized $Si_{18}H_{12}$ cluster of only 9.93 eV. According to the authors' definition of this SE (see equation above their Table 3), however, the SE decreases with decreasing binding energy $E(Si_{18}H_{12})$ when using the same reference molecule which is coherent with our simple SE definition at the beginning of this section. Since the nonoptimized (single point) $Si_{18}H_{12}$ cluster is clearly less stable than the optimized one, its binding energy is lower, and therefore, the single point SE, $SE(Si_{18}H_{12}-SP)$, should be smaller than the one for the optimized structure.

Using the same level of theory as the authors, we find an energy difference of 1.84 eV between the optimized and the nonoptimized structures yielding a SE(Si₁₈H₁₂–SP) value of only 8.09 eV (instead of 11.78 eV). This lower SE also makes intuitively sense since the nonoptimized structure has a larger central ring diameter and a larger volume than the optimized one (see Fig. 1 Ref. [[12]]). Using the authors definition, we consequently find a lower bound for the SE for Si₁₉H₁₂ of only 8.09 – 5.36 = 2.73 eV which is quite comparable to the SE value given by Earley for Si₂₀H₂₀ of 1.73 eV²³ and to the one calculated by the authors for Si₂₉H₂₄ of 1.30 eV.

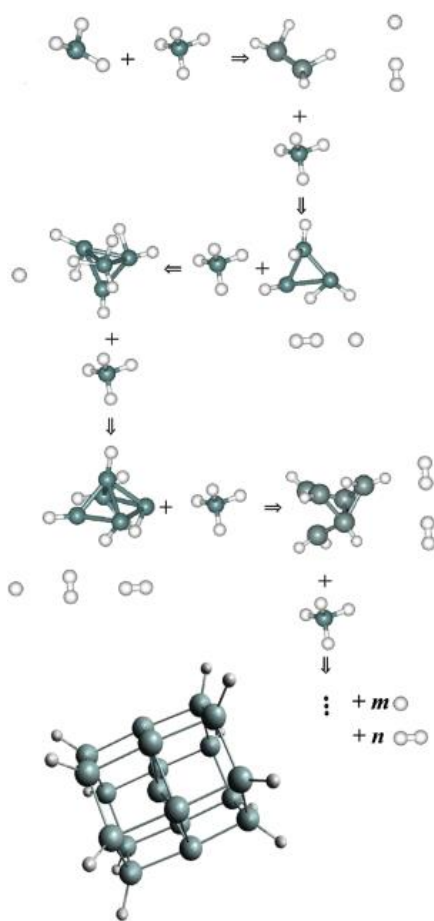


Figure 1. Starting out from a SiH₃ radical, subsequent reactions with silane molecules lead to the growth of hydrogenated silicon clusters; reactions with H-atoms heat up the growing structure permitting it to overcome barriers, whereas collisions with hydrogen molecules cool it down ultimately leading to the self-assembly of the highly symmetric Si₁₉H₁₂ nanocrystal. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Consequently, the authors do not show any evidence for a SE exceeding 2.73 eV. Since their entire article is anchored on these SE calculations, the authors cannot make any conclusions concerning the stability of the symmetric $\text{Si}_{19}\text{H}_{12}$, nor about possible isomerization, fragmentation, or autoionization processes, nor about guesses concerning the possibility for self-assembly in a realistic plasma reactor.

Finally, despite their completely different appearance, the two alternative isomers shown in Figure 4 of Ref. [[12]] have roughly the same number and nature of Si–Si bonds as the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal in question; that is, according to a rough natural bond orbital (NBO) analysis, their bonds exhibit quite the same states of hybridization, bond orders, and electron-deficiencies. Therefore, if the SE calculation brought forward by the authors of Ref. [[12]] had been valid for our symmetric nanocrystal, it would have been equally valid for their alternative isomers. Applying, thus, exactly the same procedure with the same tetrahedral reference compounds, we find strain energies for their two isomers that actually exceed the one of our symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal by 2.77 and 3.42 eV, respectively; since, with the same reference compounds, the SE increases the same way as the binding energy according to the SE definition given in Ref. [[12]]. This conclusion, however, does not seem to be correct since those isomers do not contain any apparent ring structures and since they have considerably larger volumes than our nanocrystal demonstrating once again the meaningless of any SE calculations when the precise nature is not conserved for all bonds between the reference molecule and the ones of interest.

Evidence for nondestructive strain and thermal stability

Any molecular ring system is subject to more or less strain. As we have discussed above, SE calculations can only lead to meaningful quantitative results under the condition that a suitable “strain-free” reference compound has been identified. Since we are aware of the inherent difficulty to find such a reference molecule for our electron-deficient $\text{Si}_{19}\text{H}_{12}$ nanocrystal, we would like to list several reasons suggesting that the encountered SE does not endanger the thermal stability of our $\text{Si}_{19}\text{H}_{12}$ cluster:

- The symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal is **not** the result of inserting an additional Si atom in the center of the $\text{Si}_{18}\text{H}_{12}$ cluster as it has been wrongly presented in Ref. [[12]].^{2, 5, 6, 10} Instead, it is the result of a dynamical self-assembly growth process taking place under realistic experimental plasma conditions (see Fig. 1). The underlying molecular dynamics simulations were first accomplished with semiempirical potentials^[2, 3, 5, 6] and then with *ab initio* methods.^{9, 10} To this end, silane SiH_4 molecules react with an initializing SiH_3 radical. Between subsequent encounters with two silane molecules, chemical reactions with H-atoms heat the growing structure permitting it to overcome energy barriers and to release possible strain while collisions with H_2 molecules cool the cluster down to room temperature. If any significant strain had built up by the addition of a silane molecule, the growing cluster would have had a sufficient amount of time to release this strain before its reaction with the next silane molecule.
- We have used AIMD simulations to excite different vibrational modes of the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal with an energy of 0.5 eV. Whatever mode was excited, it transferred its kinetic energy to THz oscillations of the center Si atom within about 7 ps. Since we know that the nanocrystal in question is the most vulnerable at the central hexagon,² we excited one of its silicon atoms in a direction perpendicular to the THz oscillation direction of the endohedral silicon atom and displayed the result in a movie that can be found in the Supporting Information section. As can be seen in the movie, there is so much transitional movement of all atoms induced by the artificial excitation that any major strain would have been released before the energy is transferred to the endohedral silicon atom. This process is very similar to the one previously discussed in detail^[10] and does not lead to any isomerization or fragmentation. In the same sense, we have already shown that externally excited oscillations of the endohedral Si atom even with extremely large amplitudes do not damage the nanocrystal.¹⁰
- Instead of exciting individual vibrational modes, we have also heated the entire symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal to extreme temperatures in two different manners: one with a simple

thermostat^[2] and one by excessive reactions with H-atoms.¹¹ In both cases, the nanocrystal kept its initial structure until temperatures above 1000 K and a phase transition to the liquid state at about 1550 K could be observed which is very close to the melting point for bulk silicon of 1687 K. Since temperatures above 1000 K should have facilitated a possible release of stored SE, we might suggest that the presence of a destructive amount of strain can be excluded.

- We would also like to comment on the erroneous assumption made in Ref. [[12]] that any nanocrystal strain is necessarily released to isomerization, fragmentation, or autoionization processes: While we can immediately rule out the first two mechanisms for the Si₁₉H₁₂ nanocrystal based on our AIMD simulations,^{7, 10, 11} we like to supply published experimental evidence for the third process. Since it is not possible to measure internal strain directly, we like to refer to two recent experimental studies where nanocrystals have been exposed to extremely high external strains, but no indication of any possible SE release to autoionization or fragmentation processes was observed.^{24, 25} Only at the most extreme strain conditions, nanocrystals show breathing modes eventually being followed by ultrafast disordering and melting. From the available data, however, we cannot determine with certainty whether the latter processes are triggered by the presence of the extremely high strain or by the employed photoexcitation mechanism. In any case, those structural changes take place on a subpicosecond timescale, which would have made them readily observable in our simulations if they had taken place.
- In one of those recent studies, it was experimentally demonstrated that strain can be used to transform silicon nanocrystals into a material with fundamental direct band gap.²⁴ In this work, the used strain was high enough to increase the photon emission rate of the strained silicon nanocrystals by a factor of 10,000 without making them suffer any of the destructive transformations predicted in Ref. [[12]]. We have displayed the absorption spectra calculated for the nearly strain-free Si₂₀H₂₀ fullerene and the highly symmetric Si₁₉H₁₂ nanocrystal in Figure 2. The resulting oscillator strengths are quite comparable for the two clusters. While the strongest

transition line for the symmetric $\text{Si}_{19}\text{H}_{12}$ is about twice as strong than for the nearly strain-free fullerene, it is not a matter of four orders of magnitude which could have indicated substantial strain which, however, would not have been necessarily released.²⁴ The extension of the absorption spectra toward longer wavelengths can be attributed to the aromatic-like character and not to possible strain in the ring structure of the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystals since we have seen the same spectral behavior in all asymmetric isomers.¹¹

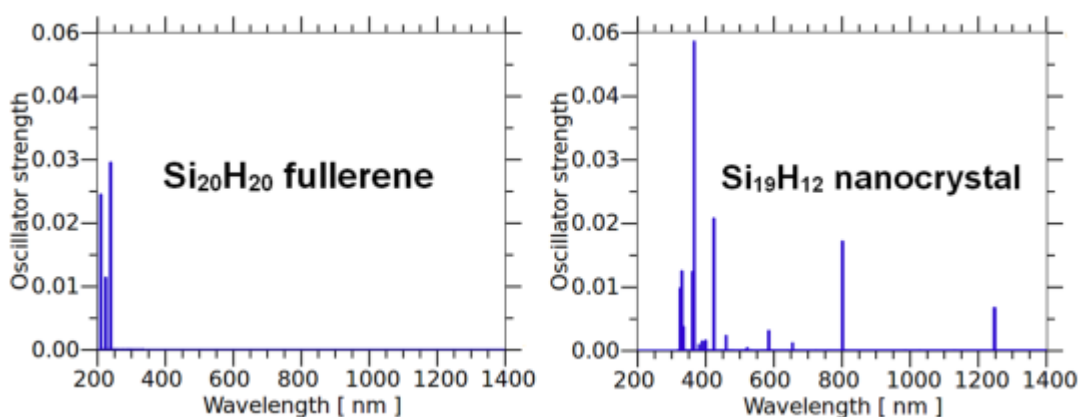


Figure 2. Optical absorption spectra calculated for the nearly strain-free $\text{Si}_{20}\text{H}_{20}$ fullerene and the highly symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal.

In conclusion, we predict that the highly symmetric plasma-born $\text{Si}_{19}\text{H}_{12}$ nanocrystal is sufficiently stable for possible device fabrication inside of a realistic low-temperature plasma reactor.

Tetrahedral versus nontetrahedral structures

In general, one can safely assume that tetrahedral silicon clusters have two electrons per bond. Nontetrahedral clusters, however, often possess over-coordinated silicon atoms; that is, Si atoms with more than four covalently bonded neighbors. This overcoordination leads to longer Si–Si bonds due to the resulting electron-deficiency. To reinforce this idea of electron-deficiency, we have displayed the electron density calculated for the top and the central hexagon of the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal in Figure 3.²⁶ Based on the used color code, one can readily estimate that the ratio of electron densities for Si–Si bonds in the top hexagon relative to the

ones in the central hexagon and relative to the Si–Si bonds of the endohedral Si atom with its six neighbors behave roughly like 2.0 to 1.6 to 1.0, which is in perfect agreement to our previous conclusions based on NBO analyses concerning the number of electrons per bond for these three cases.⁸ It is exactly this variety of different bonding schemes within the same nanocrystal that makes the identification of a suitable reference molecule so difficult for the meaningful application of homodesmotic reactions for SE calculations.

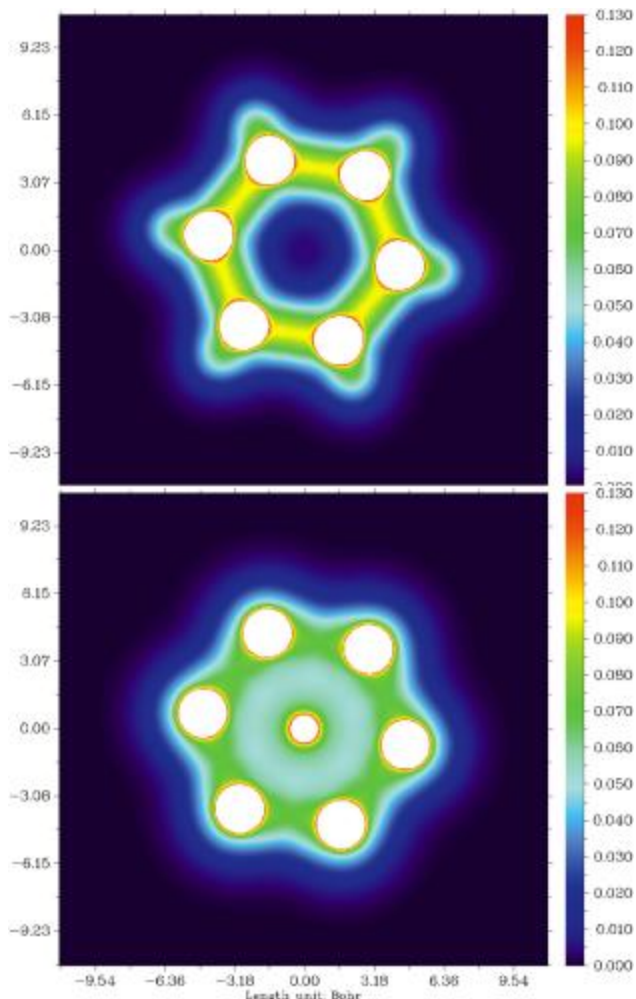


Figure 3. Electron density maps calculated for the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal in the planes of the top (upper panel) and the central hexagon (lower panel) clearly showing the electron-deficiency of the Si–Si bonds for the latter one.

Throughout Ref. [[12]], the virtue of tetrahedral bonding for ultimate cluster stability is praised. Nevertheless, the authors conclude their work by presenting two particularly stable isomers that are very

far from being tetrahedral (see Fig. 4). Performing actually exactly the same NBO analysis²⁷⁻²⁹ for those two isomers as for ours at a MP2/6-311++g(d,p) level of theory reveals strongly electron-deficient bonds (down to 1.49 electrons per bond), different hybridization states (between $sp^{1.5}$ and sp^{18}), strong stabilization energies (up to 229 kcal/mol), and high NICS values (up to -22 ppm); in addition, we find magnetically induced currents of up to 44 nA/T. All those findings clearly indicate that the alternative isomers of Ref. [[12]] are also electron-deficient, nontetrahedral, ultrastable, and aromatic.

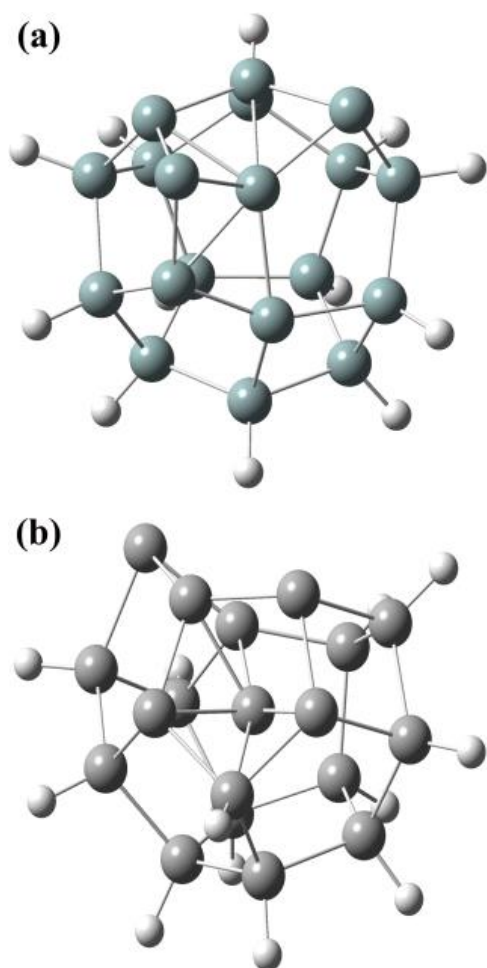


Figure 4. Two asymmetric $Si_{19}H_{12}$ isomers as suggested in Ref. [[12]] clearly displaying their nontetrahedral nature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the same sense, the section concerning the transformation from tetrahedral to half-planar conformation in model CH_4 and SiH_4 molecules in Ref. [[12]] is pedagogically interesting, but without any

relevance to the present discussion since the authors only considered again fully occupied two-electron bonds, but no electron-deficient bonds that play the dominant role in the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal.

In summary, besides the elementary mistakes outlined above, we like to point out that most erroneous conclusions in Ref. [[12]] can be traced back to the fact that throughout this work (except for the Gaussian calculations), the authors considered all bonds in the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal as being fully occupied by two electrons. Nowhere the highly delocalized nature nor the electron-deficiency of this nanocrystal was considered although those are responsible not only for the outstanding new features, but for the very existence of this new family of overcoordinated hydrogenated silicon clusters.

Conclusions

While all molecular ring structures are subject to more or less strain, we have shown evidence that the strain in the symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal is too small to cause any isomerization, fragmentation, or autoionization under typical conditions in a plasma reactor. We have based this conclusion on the fact that the nanocrystal forms by self-assembly during an atom-by-atom nucleation process at room temperature in a realistic plasma reactor; that selective excitation of any of its vibrational modes always leads to a nondestructive internal energy transfer resulting in THz oscillations of its endohedral Si atom; that thermal heating only yields a loss of its symmetric structure above 1000 K; that extremely strained nanocrystals do not show any strain release to isomerization, fragmentation, or autoionization according to recent experiments; and that high strain is expected to transform silicon nanocrystals in a direct-bandgap material leading to a nondestructive photo emission rate enhancement of several orders of magnitude while the oscillator strengths calculated for our symmetric $\text{Si}_{19}\text{H}_{12}$ nanocrystal do not exceed the ones for the nearly strain-free $\text{Si}_{20}\text{H}_{20}$ fullerene by more than a factor of two. We have also demonstrated that the homodesmotic reaction approach to calculate strain energies leads to completely meaningless results when the number and/or the nature of all bonds are not conserved between the products and the reactants

especially for the present case where the product is marked by extremely electron-deficient bonds and strongly delocalized electrons.

Acknowledgments

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Supporting Information for

A deeper insight into strain for the sila-bi[6]prismane (Si₁₈H₁₂) cluster with its endohedrally trapped silicon atom, Si₁₉H₁₂

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We have used *ab initio* molecular dynamics (AIMD) simulations to excite different vibrational modes of the symmetric Si₁₉H₁₂ nanocrystal with an energy of 0.5eV. Whatever mode was excited, it transferred its kinetic energy to THz oscillations of the center Si atom within about 7ps. Since we know that the nanocrystal in question is the most vulnerable at the central hexagon,² we excited one of its silicon atoms in a direction perpendicular to the THz oscillation direction of the endohedral silicon atom and displayed the result in the present movie. As can be seen in the movie, there is so much transitional movement of all atoms induced by the artificial excitation that any major strain would have been released before the energy is transferred to the endohedral silicon atom. This process is very similar to the one previously discussed in detail¹⁰ and does not lead to any isomerization or fragmentation.