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Exploring the Potential Energy Surface of Medium-Sized Aromatic Polycyclic Systems with Embedded Planar Tetracoordinate Carbons: A Guided Approach

Diego Inostroza, [1,2] Luis Leyva-Parra, [1,2] Osvaldo Yañez [3], Andrew Cooksy [4], Venkatesan S. Thimmakondu [4,*] and William Tiznado [1,*]

[1] Computational and Theoretical Chemistry Group, Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Avenida República 275, Santiago de Chile 8370146, Chile; l.leyvaparra@uandresbello.edu; dinostro92@gmail.com

[2] Programa de Doctorado en Fisicoquímica Molecular, Facultad de Ciencias Exactas, Universidad Andrés Bello, Avenida República 275, Santiago de Chile 8370146, Chile; l.leyvaparra@uandresbello.edu; dinostro92@gmail.com

[3] Núcleo de Investigación de Data Science, Facultad de Ingeniería y Negocios, Universidad de las Américas, Santiago 7500000, Chile; oyanez@udla.cl

[4] Departament of Chemistry and Biochemistry, San Diego State University, San Diego, CA, 92182-1030 USA; acooksy@sdsu.edu

* Correspondence: vthimmakondusamy@sdsu.edu (V.S.T.); wtiznado@unab.cl (W.T.)

Abstract: This study scrutinizes the complexities of designing and exploring the potential energy surface (PES) of systems containing more than twenty atoms with planar tetracoordinate carbons (ptCs). To tackle this issue, we utilized an established design rule to design a Naphtho [1,2-b:4,3-b′:5,6-b″:8,7-b‴′]tetrathiophene derivative computationally. This process began with substituting S atoms with CH^- units, then replacing three sequential protons with two Si^{2+} units in the resultant polycyclic aromatic hydrocarbon polyanion. Despite not representing the global minimum, the newly designed Si_8C_{22} system with four ptCs provided valuable insights into strategic design and PES exploration. Our results underscore the importance of employing adequate methodologies to confirm the stability of newly designed molecular structures containing planar hypercoordinate carbons.

Keywords: planar tetracoordinate carbon; silicon-carbon clusters; global minima; DFT computations; chemical bonding analysis; aromaticity

1. Introduction

In the past five decades, the scientific community has witnessed remarkable progress in understanding and exploring compounds containing planar hypercoordinate carbons (p-hyp-Cs) [1–23]. These intriguing compounds are characterized by carbon atoms connected to a minimum of four in-plane atoms. Despite initial skepticism due to their violation of the van't Hoff and Le Bel's rules, which favor the tetrahedral configuration of tetracoordinate carbon compounds [24,25], researchers have made significant strides in this field.

The exploration of compounds with p-hyp-Cs can be traced back to 1968 when Monkhorst first proposed the CH_4 transition state planar structure involved in the stereomutation of methane [26]. In 1970, Hoffmann and his team showed that the stability of the planar tetracoordinate carbon (ptC) structure could be enhanced electronically[27]. This was achieved by substituting the planar methane H atoms with either σ electron donors, which improved their involvement in electron-deficient σ bonds, or π acceptors, which helped distribute the unfavorable lone pair of the central atom. This led to the conceptualization of various molecular prototype architectures. In 1976, Collins and his colleagues theoretically introduced the first ptC-containing molecule, 1,1-dilithiocyclopropane[1].

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This was followed by the unintentional synthesis of the first ptC-containing molecule by Cotton and Millar a year later [28], marking a significant milestone in this field. These studies began a journey leading to numerous discoveries and advancements.

Inspired by the concepts offered by Hoffman and coworkers, our group proposed a method to construct planar tetracoordinate carbon (ptC) global minima (GM). This method centered around substituting three consecutive protons from an aromatic hydrocarbon with two E^{2+} dications, where E represents elements from Silicon (Si) to Lead (Pb) [29]. This substitution was designed to preserve the π-aromatic circuits inherent in the parent aromatic hydrocarbons. This strategy was initially tested on derivatives of small aromatic hydrocarbons, each featuring one or two ptCs [23,29–35]. A striking feature of these ptC systems is their global π-aromaticity and three-center, two-electron (3c-2e) E-ptC-E σ- bonds that display localized σ-aromaticity.

Exploring the potential energy surfaces (PES) of p-hyp-Cs species is essential to ensuring them as GM structures [21,23,30,34], thus supporting their experimental viability (at least in gas phase experiments) [14,36]. Consequently, devising methods to assist PES exploration is vital for discovering new viable p-hyp-C species [37–42]. Experimentally, gaseous species are spectroscopically characterized; however, theoretical research remains indispensable in gaining insights into these compounds' structural and electronic structures, especially for identifying the lowest energy structure (GM) and other relevant structures for matching between the computed and experimental spectrum, thus allowing the structural elucidation of the compound identified in the gas cloud [43].

In the study of p-hypC systems, the employment of stochastic and evolutionary algorithms is common to locate the lowest energy structures amongst the plethora of structural possibilities, thereby improving our understanding of the stability and reactivity of p-hyp-Cs compounds [21,23,29,44,45]. Numerous GM structures have been reported, including planar tetracoordinate, pentacoordinate, and hexacoordinate carbon structures [14,19,20,22,46,47]. However, the efficiency of search algorithms decreases with increasing system size due to the exponential growth of local minima to be visited [48,49]. Systems exceeding 20 atoms could present substantial challenges, and these difficulties are further amplified when they comprise more than two elements, such as Si, C, and H, in the current study. Therefore, an important question arises, how to explore the PES of candidates for GMs with p-hyp-Cs with more than 20 atoms?

In this study, we apply the design rule for systems with ptCs, as mentioned above, to the design of a Naphtho[1,2-b:3,4-b′:5,6-b″:7,8-b‴]tetrathiophene derivative, chosen for their aromatic peripheral pentagonal rings. Moreover, a similar strategy was employed last year, beginning with the [6]radialene benzo[1,2-c:3,4-c0:5,6-c00]trithiophene, which enabled us to design a GM harboring three ptCs [29]. The system we design here, Si_8C_{22}, has an isomer with four ptCs that exhibits aromaticity but does not correspond to the GM. Nevertheless, examining this system has been beneficial for testing the design rule and a guided strategy for exploring its PES, given the complexity of this task for such a large system using conventional techniques.

Consequently, our results emphasize the importance of employing appropriate methodologies to validate the thermodynamic and kinetic stability of newly computationally designed structures containing p-hyp-Cs.

2. Computational Details

Our guided exploration of the PES of the Si_8C_{22} started using the coronene ($C_{24}H_{12}$) as a starting structural template, applying a dual-stage atomic exchange process. Initially, a hydrogen-to-silicon atomic substitution was executed, succeeded by a swap where four silicon and two carbon atoms were removed to achieve the intended stoichiometry (Refer to Figure 3). Employing the AM1 method [50], we methodically scrutinized an exhaustive set of 993 structures through single-point computations to pinpoint energy-favored structures. Isomers displaying energies beneath 50 kcal·mol^{-1} underwent subsequent geometric optimization at the PBE0 [51]/SDDAll [52–56] level. Then, structures maintaining energies below 30 kcal·mol^{-1} were refined at the PBE0-D3 [57]/Def2-TZVP [58] level, complemented by vibrational frequency assessments to affirm their status as true

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PES minima (Figure S1). All these calculations were performed with the Gaussian16 (Revision B.01) program [59].

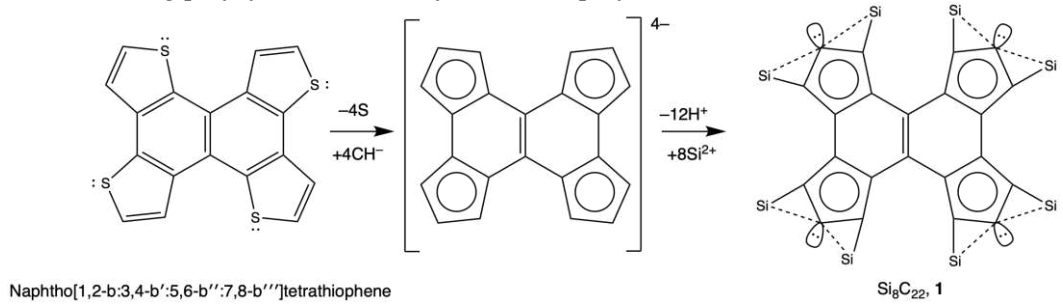
We computed current densities utilizing the GIMIC program [60,61] that implements the gauge-included atomic orbital (GIAO) method [62] at the PBE0-D3/Def2-TZVP level, considering an external magnetic field oriented perpendicular to the molecular plane. In our analysis, diatropic (aromatic) and paratropic (antiaromatic) ring currents circulate clockwise and counterclockwise, respectively. Visualization of these currents was performed with Paraview 5.10.0 software [63,64], and ring current strength (RCS) was determined after considering various rectangular integration planes that intersected the bonds of interest, originating from the center of the rings (Refer to Figures S2 and S3). The GIMIC program's integration process employs the two-dimensional Gauss-Lobatto algorithm [65]. Positive and negative RCS values represent diatropic (aromatic) and paratropic (antiaromatic) ring currents, respectively, while values near zero indicate a non-aromatic character [66]. The different ring current circuits have been determined by analyzing the current strength profiles across the integration planes (see Figures S2, S3), following the strategy previously proposed elsewhere [66–68].

Chemical bonding analyses employed several methods: Wiberg bond indices (WBI) [69], natural population analysis (NPA) [70], and the adaptive natural density partitioning method (AdNDP) [71,72]. These methodologies are anchored in the natural bond orbital (NBO) method and were executed using the wavefunction derived at the PBE0-D3/Def2-TZVP level. WBI and NPA computations were facilitated with the NBO 6.0 code[73], while the AdNDP analysis was carried out with Multiwfn 3.8 [74]. Molecular structure and AdNDP orbitals were visualized using CYLview 2.0[75] and VMD 1.9.3 [76].

3. Results and Discussion

3.1. Design of the Si_8C_{22} Cluster Incorporating Four ptCs

This research delves into the intricate processes of designing and examining the PES of polycyclic systems comprising over twenty atoms featuring ptCs. To address this challenge, we employed a proven design principle [23,29–35], to computationally formulate a derivative of Naphtho[1,2-b:4,3-b′:5,6-b″:8,7-b‴]tetrathiophene. This design procedure initiated substituting sulfur atoms with CH^- units. Then a sequential triplet of protons is replaced with a pair of Si^{2+} units within the resulting polycyclic aromatic hydrocarbon polyanion (see Scheme 1).



Scheme 1. Design of Si_8C_{22} ptC system starting from the Naphtho[1,2-b:3,4-b′:5,6-b′′:7,8-b′′]tetrathiophene (left) to build $C_{22}H_{12}^{4-}$ and finally the ptC candidate (right).

Despite not achieving the global minimum (GM), the resultant cluster (**1**) is a local minimum on the PES. It allowed us to assess a simple but effective strategy to explore its PES (see below). Our findings accentuate the necessity of rigorous methodologies to validate the stability of novel structures featuring p-hyp-Cs.

A crucial prerequisite for the design of ptC embedded aromatic rings is their inherent aromatic character. A recurring trait among the previously reported global minima (GMs) of these systems includes global, semilocal, and local π-aromaticity, the latter two present in fused rings, supplemented by local σ-aromaticity provided by the delocalization of two electrons in the E-ptC-E delocalized bond, where E represents Si in this study. Thus, our analysis necessitates an in-depth

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evaluation of this aromaticity. To accomplish this, we assessed the magnetically induced current density. We employed current strength profiles to identify the ring current circuits and their respective strengths (nA/T), as depicted in Figure 1, following a strategy established previously [66–68].

For comparative purposes, Figure 1 also presents analyses for two formerly reported systems, one derived from benzene ($Si_2C_6H_2^+$) and another from cyclopentadienyl anion (Si_3C_5). Notably, these monocyclic rings display a pronounced diatropic ring current (15.3 and 12.0 nA/T) distributed predominantly around carbon rings. Local diatropic ring currents around ptC (8.2 and 6.1 nA/T), possibly linked with local Si-ptC-Si delocalization, and paratropic ring currents at the molecular rings' center, albeit less intense, are also discernible. These observations align with those reported earlier for these systems [30–33]. System 1's current density analysis reveals a strong diatropic global ring current (12.7 nA/T) and much fainter local diatropic ring currents (2.3 and 2.5 nA/T). Local currents around the ptCs, and weak paratropic local currents within the local rings, are also identified. These findings, therefore, affirm the robust aromatic character of System **1** following our design strategy.

However, affirming System **1** as the most stable structure for the Si_8C_{22} combination requires further verification. This validation can only be achieved by comprehensively scanning the PES of the Si_8C_{22} cluster, as elucidated in the subsequent section.

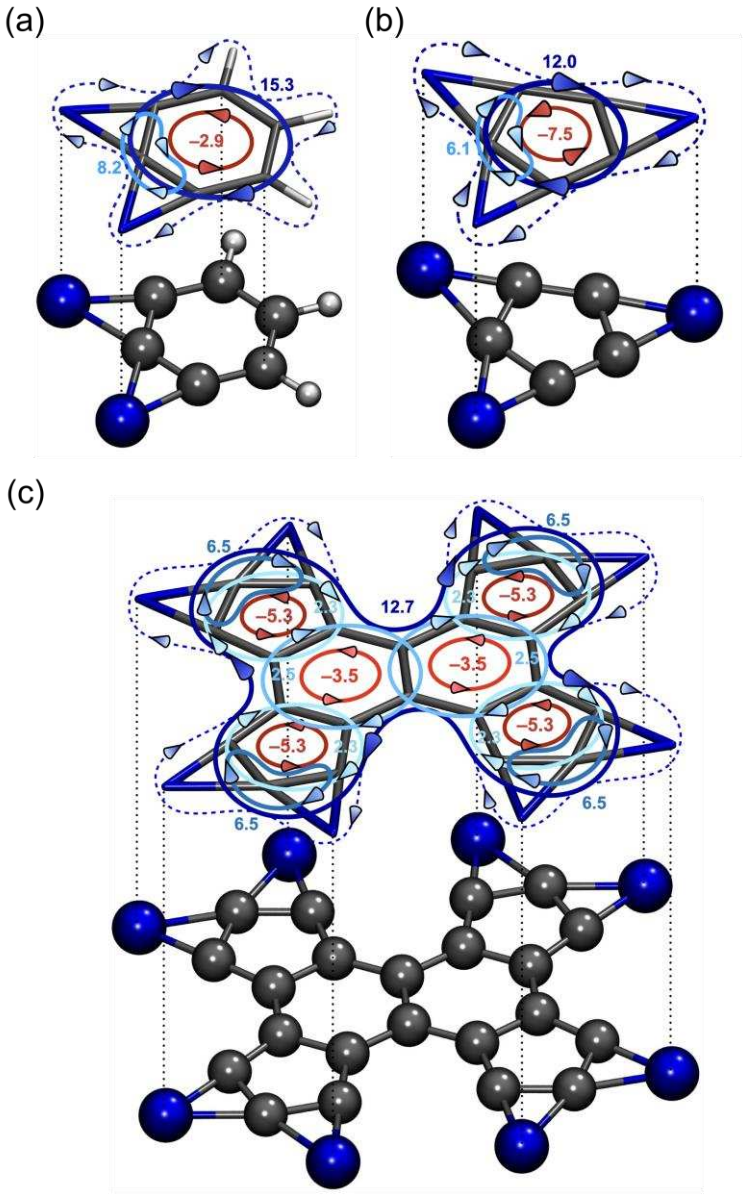

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Figure 1. Schematic depiction of the identified ring current circuits (noted with their corresponding strengths in nA/T) for aromatic hydrocarbon derivatives featuring ptCs. Subfigures include: a) benzene derivative ($Si_2C_6H_3^+$), b) cyclopentadienyl anion derivative (Si_3C_5), c) Naphtho[1,2-b:3,4-b′:5,6-b″:7,8-b‴′]tetrathiophene derivative(S_8C_{22}).

Our previous analysis revealed that the magnetic response analysis of compound **1** identified it as an aromatic system. However, what can we infer about this system from the perspective of its chemical bonding? The Adaptive Natural Density Partitioning (AdNDP) analysis offers an instructive portrayal of the chemical bonding within this species. As depicted in Figure 2, the AdNDP technique uncovers the lone-electron pairs on each Si atom, the C-C σ-bonds forming the C_{22} backbone, and the C-Si σ-bonds linking the C-periphery with Si atoms. Additionally, it unveils the delocalized Si-ptC-Si three-center two-electron (3c-2e) σ-bonds, a defining feature of these species.

Moreover, 13 delocalized π-bonds accounting for 26 π-electrons are spread across the system. If one were to draw parallels with the current analysis, these could be partitioned into local and global groups, in both cases adhering to Hückel's 4n+2 rule for aromatic systems, demonstrating their aromaticity. Thus, the AdNDP analysis confirms that compound **1** maintains the bonding patterns observed in its predecessors, featuring ptCs integrated into an aromatic ring. This interpretation of chemical bonding also agrees with the Wiberg bond index (WBI) analysis, as reported in Figure S4.

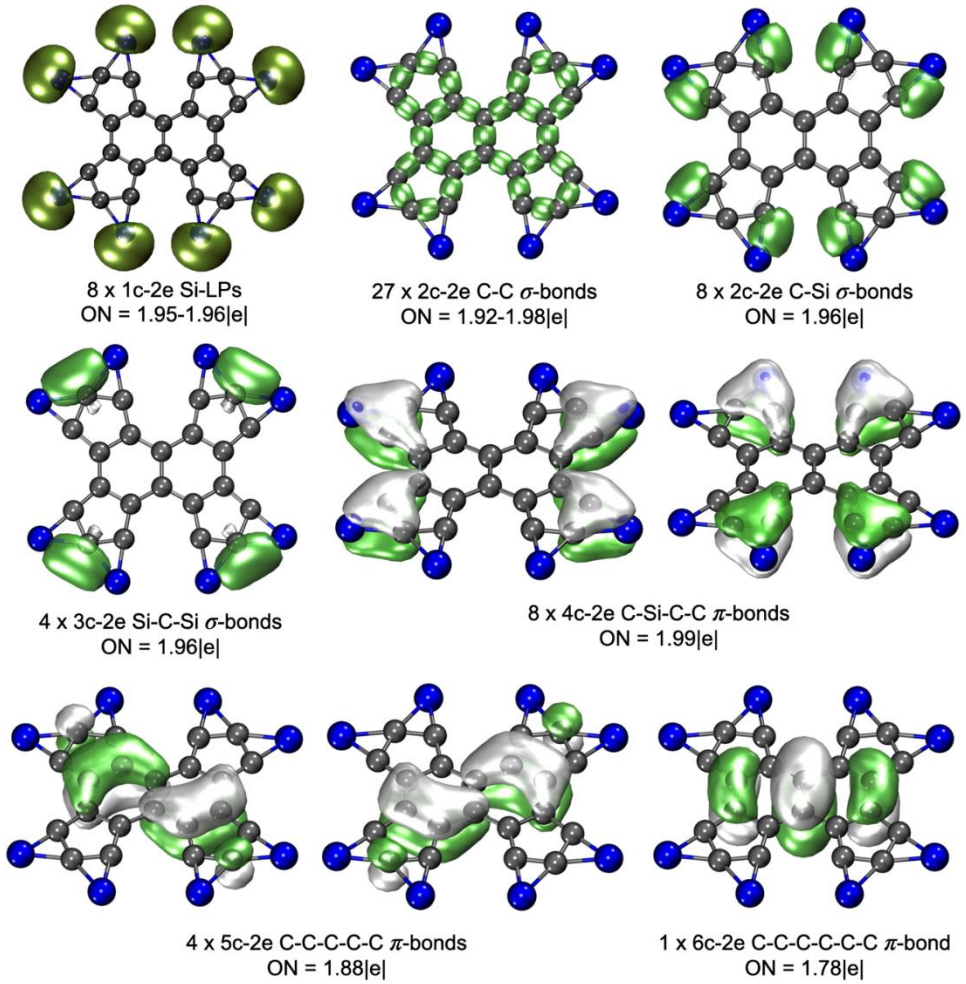

Figure 2. AdNDP analysis of **1** at the PBE0-D3/Def2-TZVP level. ON stands for occupation number. Carbon=gray, silicon=blue.

3.2. Potential Energy Surface Exploration of the Si_8C_{22} Cluster

As commented in the introduction, exploring the PES of medium-sized clusters using commonly implemented methods such as genetic algorithms or stochastic procedures is challenging due to the

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computational resources required, which many research groups might find prohibitive. This is because many candidate structures need to be evaluated and optimized locally, i.e., using density functional theory (DFT) methods and an adequate basis set.

To overcome these hurdles, we leveraged what is commonly referred to as "chemical intuition," using structural and chemical bonding information from prior studies on analogous systems to generate our candidate population. However, the success of strategies based on chemical intuition to explore the PES of atomic clusters depends on the information used as a guide. In the past, we used the best minima derived from a stochastic search or evolutionary methods, which were subsequently slightly altered (moving atoms to generate a new structure) [77]. With this approximation, we enriched the variety of local minima close in energy to the GM by identifying missing structures in the evolutive or stochastic search. Besides, in the case of systems featuring p-hyp-Cs embedded in polycyclic aromatic hydrocarbons, we succeeded by performing substitutions and permutations on related and well-characterized polycyclic hydrocarbon structures to the system under study [29]. This method allowed the sampling of a wide range of polycyclic structures with randomness introduced by the permutations and substitutions. Thus, we will employ this strategy here.

It is crucial to mention that the used approach is successful only when we ensure that we sample the correct region of the PES, i.e., where the global minimum should ideally be found. While we cannot guarantee this 100%, our prior studies suggest it is an adequate method for this system. Building on these considerations, we illustrate the procedure employed for the PES exploration of Si_8C_{22} in Figure 3. We selected coronene ($C_{24}H_{12}$) as the starting template and stochastically removed two carbon atoms. As the figure represents, we replaced H atoms with Si, resulting in 12 Si atoms, from which we randomly removed four. To fulfill the carbon atoms in the interest system. By this procedure, we generated 993 structures whose energy was computed using a semiempirical method; then, the best structures in a range of 50 kcal·mol^{-1} were optimized via a DFT method using a small basis set. Finally, we refined the best structures within a 30 kcal·mol^{-1} range at a higher level (for more details on the used methods, refer to the computational methods section). Figure 3 displays the best structures identified through our exploration. This approach allowed for a thorough yet resource-conscious exploration of the PES of Si_8C_{22}, offering valuable insights into the energetically preferred structures for this combination. Regrettably, Structure 1 exhibits considerably higher energy than the best-identified structure for the Si_8C_{22} combination. Nevertheless, this study underscores the essentiality of employing suitable techniques to ascertain that the designed cluster corresponds to the global minimum. This prerequisite critically influences its potential viability in the gas phase.

An intriguing question that persists is why **1** is not a good minimum on the potential energy surface (PES). A plausible explanation may be uncovered by examining its computationally designed structural counterpart, the $C_{22}H_{12}^{4-}$ tetra-anion, which is stabilized by four Li^+ counterions. As reported in Cartesian coordinates (in Table S1), the C_{22} skeleton in $Li_4C_{22}H_{12}$ does not lay flat, in contrast to the planar configuration in System **1**, possibly due to the rigidity imparted by the bridged Si-C bonds. Consequently, this flatness could strain the C_{22} skeleton, ultimately rendering the structure of **1** with four ptCs energetically unfavorable.

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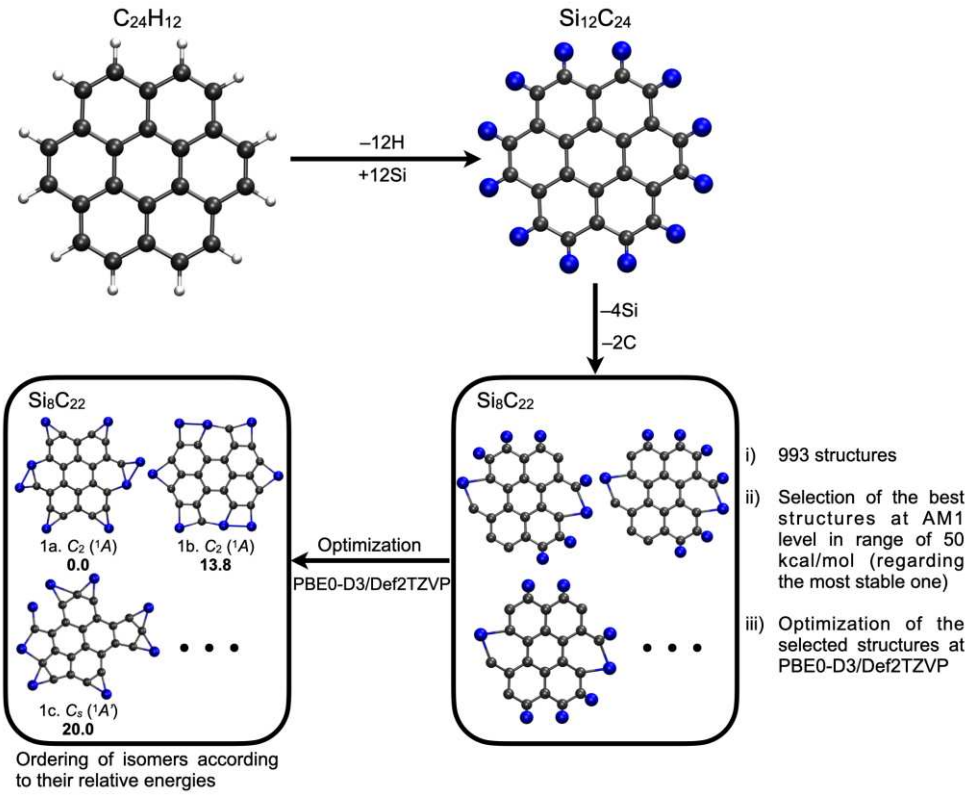

Figure 3. Schematic representation of the strategic approach for exploring the Si_8C_{22} cluster's potential energy surface.

3. Conclusions

In this research, we have utilized a previously suggested strategy to design a cluster, termed **1**, with the formula Si_8C_{22} featuring four planar tetracoordinate carbons (ptCs). We adopted Naft[1,2-b:3,4-b':5,6-b'':7,8-b''']tetrathiophene as the base structure, wherein sulfur atoms were initially replaced with CH^- units. Subsequently, two Si^{2+} units replaced three sequential protons. Although this strategy has proven successful in designing global minima featuring ptCs in the past, our findings demonstrate that **1** does not represent the global minimum. Instead, it is a local minimum, positioned over 30 kcal/mol above the lowest energy structure identified in this study.

An essential contribution of our work lies in assessing a novel yet straightforward methodology for exploring such systems' potential energy surface (PES) using known polycyclic hydrocarbons as template structures. Specifically, we used coronene, which facilitated evaluating a series of designs through substitution, elimination, and permutation of atoms.

The reliability of the minima identified through this approach is corroborated by earlier studies where it was compared with evolutionary methods. Our findings underscore the significance of employing appropriate ways to navigate the PES when designing structures with planar hypercoordinate carbons, particularly pertinent for intermediate-sized forms, like **1**, where conventional stochastic or evolutionary methods can be challenging to implement. Note that the manual approach may be subject to biases that obstruct identifying the best structures.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Minimum energy isomers of Si_8C_{22} and their respective point group symmetries and spectroscopic states. Relative energies are shown in kcal·mol^{-1} at PBE0-D3/Def2-TZVP levels including zero-point energy (ZPE) corrections. Figure S2: Vector plots visualization of the current density in diverse planes of the Si3C5, Si2C6H3+ and Si8C22 cluster. Diatropic currents are assumed to circle clockwise. Figure S3: Top view of integration planes considered to average the profile RCS for Si3C5, Si2C6H3+ and Si8C22 (up) and the RCS pro-files along the different integration planes (down). Figure S4: Bond length in (black), natural charges (red and blue) and Wiberg bond indices (green) for Si8C22 at the PBE0-D3/Def2-TZVP level of

theory. Table S1: Cartesian coordinate of the C22H124– and Si8C22 systems calculated at the PBE0-D3/Def2-TZVP level of theory.

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