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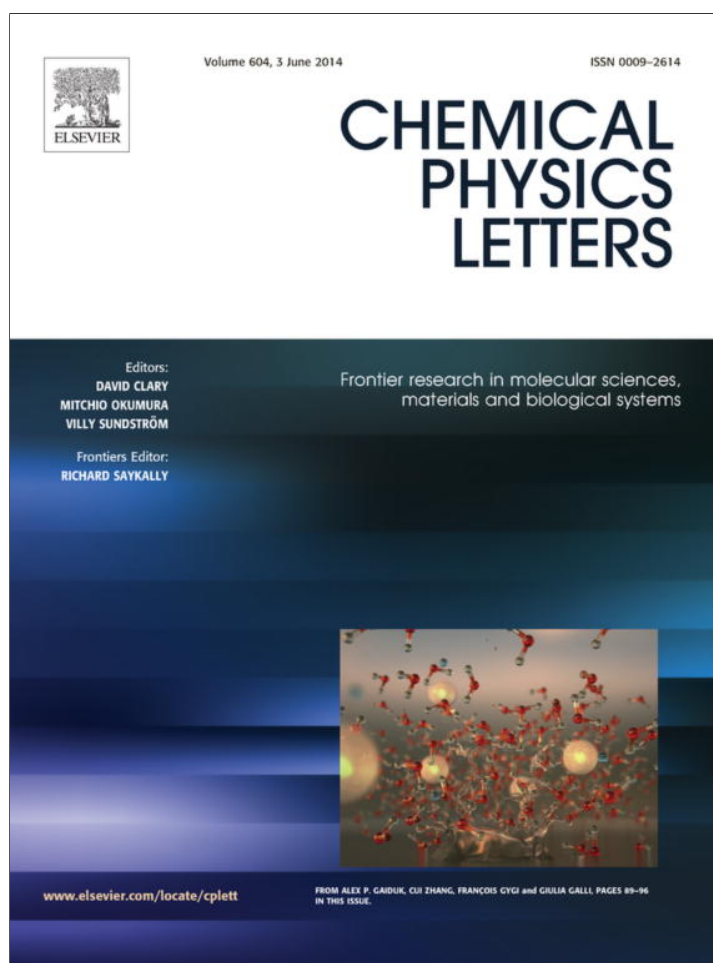


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journal homepage: www.elsevier.com/locate/cplettStability analysis of lithio-silicon $\text{Si}_{10}\text{Li}_8$ clusters: Planar bicyclic ring vs. three-dimensional structures

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ABSTRACT

After exploration of the potential energy surface for the stoichiometry of $\text{Si}_{10}\text{Li}_8$ a three-dimensional motif was found as the most stable in comparison with planar and quasi-planar structures. The new minimum can be seen as the resulting of the interaction of three fragments: $\text{Si}_2 \cdots \text{Li}_4 \cdots \text{Si}_8\text{Li}_4$ stabilized by strong electrostatic interactions. In order to understand the stability both polarizability and aromaticity were studied. In general, the structural transition from planar or quasi-planar to three-dimensional structures increases the stability while decreases the polarizability of the system, in agreement with the minimum polarizability principle.

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1. Introduction

Carbon and silicon are members of group IV of the periodic table; although they exhibit several similarities their chemistry can be quite different. While carbon is essential for life, silicon is for modern electronic technology [1–6]. One of the well-characterized carbon-containing compounds is the aromatic rings or arenes [7–9], but it is possible to obtain ionic interactions in carbon compounds, i.e. if hydrogen atoms are replaced by lithiums in benzene, it is possible to destroy cyclic carbon backbone yielding a new three-dimensional minimum in which aromaticity is not enough to preserve the symmetry of the new molecule [10]. Concomitantly, the characterization of structural, electronic and stability properties of silicon analogues emerge as an interesting issue to be addressed, which, on the other hand, could provide guideline for the development of organic and inorganic semiconductor materials.

Silicon clusters have been experimentally and theoretically investigated [11–16]. The main controversy concerns the structural motif, i.e. two- (fully or quasi-planar) vs. three-dimensional arrangements. While some studies have indicated that silicon clusters preferentially adopt three-dimensional polyhedral structures favoring the σ -bonding pattern; others studies have shown that π -aromaticity is the main driving force behind the stabilization of the two-dimensional with planar bicyclic silicon ring backbone [11–18].

Zdetsis et al. reported a π -bonded D_{2h} symmetry as the most stable structural isomer of Si_6Li_6 cluster. This geometrical motif has a

pair of Li atoms positioned one above and other below of the six-membered silicon ring whereas the remainder four Li atoms are positioned in the plane between two adjacent silicon atoms forming a bridge bond type. The stability of this silicon-benzene analogue was explained in terms of the high aromaticity of the Si_6 ring. In an earlier work, Santos and Fuentealba [19] analyzed the electronic structure of silabenzenes, $\text{Si}_n\text{C}_{6-n}\text{H}_6$, and lithiated silabenzenes, Si_6Li_6 , $\text{Si}_6\text{Li}_8^{+2}$ series by using topological analysis of electron localization function (ELF), finding a Si_6Li_6 cluster (D_{6h} symmetry) as an aromatic compound, where each Li atom form a bridge bond type. Later, Santos et al. [20] found a new structural motif for Si_6Li_6 , which is completely different from the previously reported structures (D_{2h} and D_{6h}). This geometrical motif is formed by the interaction between a silicon tetrahedron unit with a silicon dimer separated by four Li atoms unit, the two remainder Li atoms are localized on the tetrahedron unit, and their bond types give the stability order. Moreover, the minimum polarizability principle was fulfilled, concluding that three-dimensional structures are more stable than those planar or quasi-planar due to their compactness.

In a recent study, a set of lithiated polycyclic silicon rings was analyzed; Jing et al. [21] proved that the structures with Li atoms above and below the silicon rings are the most stable isomers. Specifically, for the stoichiometry of $\text{Si}_{10}\text{Li}_8$, the authors proposed three isomers based on Si_{10} core labeled as D-1, D-2, and D-3 in Figure 1. It can be noted that D-3 is a fully planar structure whereas D-1 and D-2 have Li atoms positioned above and below the silicon backbone and the four remainder Li atoms are in the plane interacting with alternate and adjacent silicon atoms by bridge bond type, (here we will consider them as quasi-planar structures). D-1 was predicted as the most stable isomer because the π -electron delocalization along both silicon rings, facilitated by the out-of-

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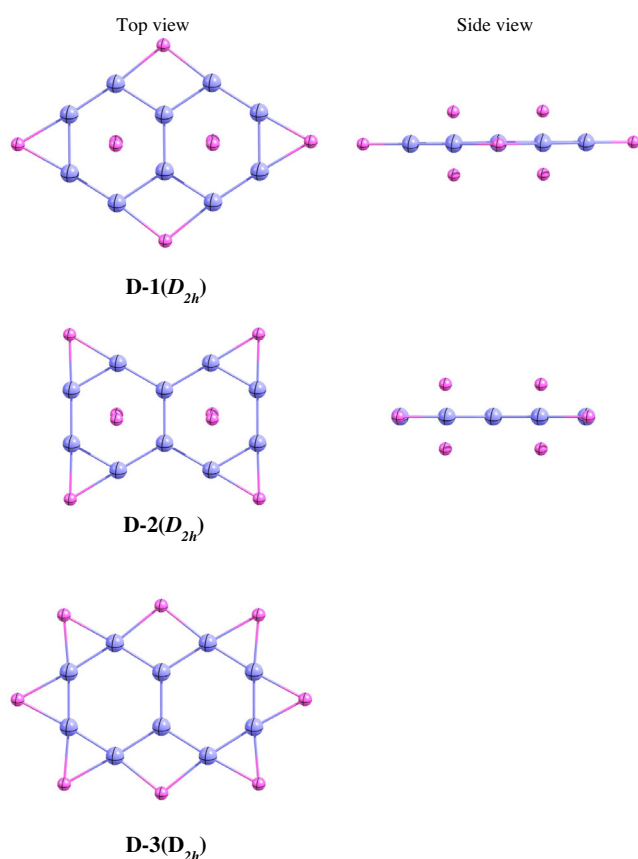


Figure 1. Reported isomers of $\text{Si}_8\text{Li}_{10}$ cluster.

plane Li atoms, can be supported by the formation of the alternate bridge bond type in the plane (which is linking the two rings).

This work proposes a new set of $\text{Si}_{10}\text{Li}_8$ isomers, including both planar (see Figure 2) and three-dimensional (see Figure 3) ones, aiming to find answers if all planar structures are mainly stabilized by π -aromaticity and what is the contribution of this criterion on the three-dimensional motifs? Or if another factor, such as the dielectric polarizability, can be behind the stabilization of these structural motifs.

2. Computational details

The procedure followed to localize the new 3D-1 and 3D-2 structures (see Figure 3) of $\text{Si}_{10}\text{Li}_8$ cluster starts with the replacement of the lithium atoms by silicon into the three-dimensional motifs previously reported for Li_{10} clusters by Yepes et al. [22]. These metallic structures were localized by a stochastic procedure through the ASCEC software and the computational details can be found in references [23–25]. The next step was a randomly saturation of the silicon clusters, formed basically by fused tetrahedral, with 8 Li atoms trying to keep a symmetrical distribution around the silicon core. Finally, full geometry optimizations of the starting structures were performed with the hybrid B3LYP exchange–correlation functional [26,27], combined with the split-valence triple- ζ basis set Def2-TZVP. This computational protocol has shown to be suitable to provide electronic energies and molecular geometries. The stationary states were confirmed as true minima through harmonic vibrational analyses. All calculations were carried out with the GAUSSIAN 03 suite of programs [28].

On the other hand, the new quasi-planar clusters D-4 to D-7 (see Figure 2) were also postulated aiming to compare with the previously reported isomers D-1, D-2 and D-3. All of these geometries were also fully optimized at B3LYP/Def2-TZVP level.

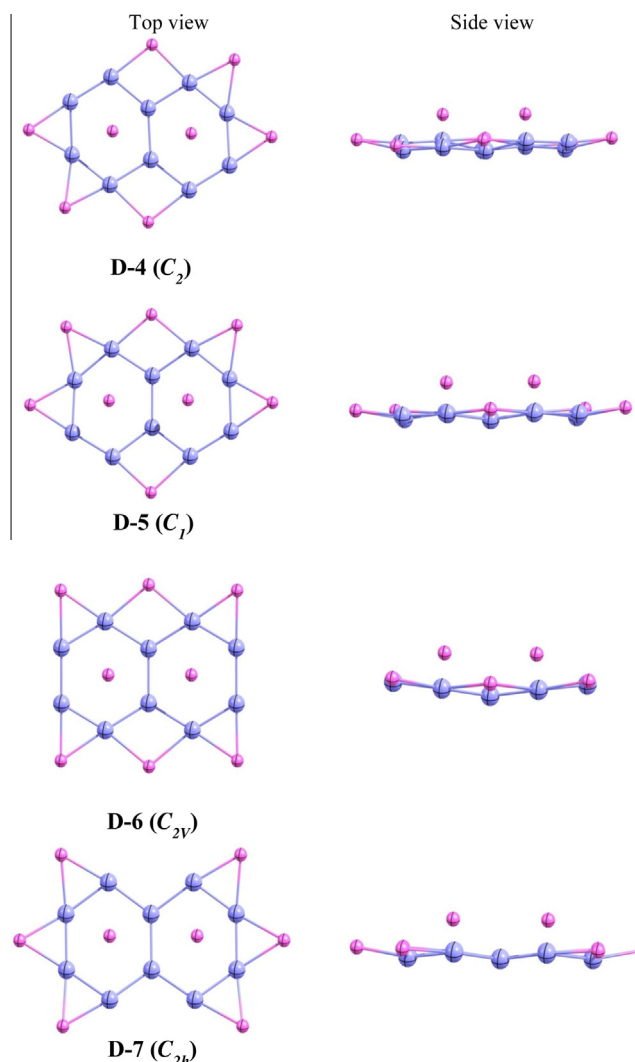


Figure 2. New quasi-planar structures of $\text{Si}_8\text{Li}_{10}$ cluster.

Aromaticity was evaluated using the topological analysis of the Electron Localization Function (ELF) [29]. In this context, Santos et al. [30] proposed an aromaticity scale based on the average bifurcation value of the ELF of both σ (ELF- σ) and π (ELF- π) contributions, which has been validated in a wide variety of systems [31–33]. The ELF study was performed for the three functions with the TOPMOD software [34] using the corresponding monodeterminantal wave function of the minima. Isosurfaces and bifurcation points have been visualized with the program MOLEKEL [35].

The clusters' stability has been rationalized through both the HOMO–LUMO gap (the hardness (η)) and the polarizability (α) in order to validate both principles the maximum hardness [36] and the minimum polarizability [37] which complement the minimum energy criterion for molecular stability. While the former asserts that, at a given temperature, molecular systems will evolve towards a state of maximum hardness, the latter affirms that 'the natural direction of evolution of any system is toward a state of minimum polarizability'.

Polarizabilities of clusters have been studied both theoretically and experimentally during the past few years [38–40]. The electric dipole polarizability α measures the response of the electron charge density of a molecule when the external potential is changed. Under an uniform electric field \vec{F} , the dipole polarizability tensor, α_{ij} , is defined as:

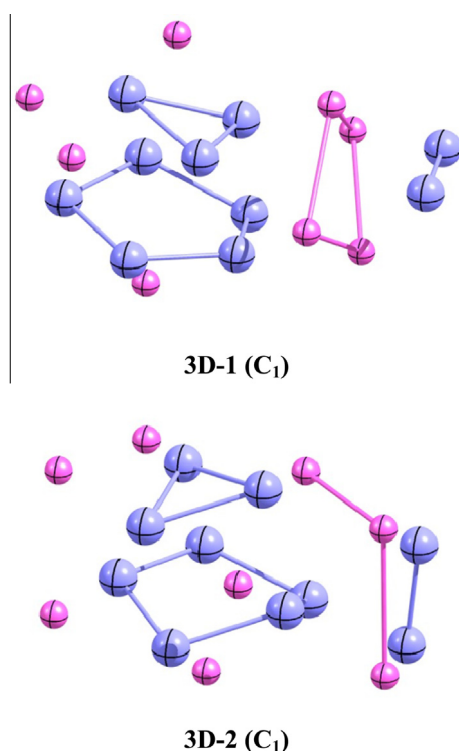


Figure 3. Most stable three-dimensional structures of $\text{Si}_8\text{Li}_{10}$ cluster.

$$\alpha_{ij} = - \left(\frac{\partial^2 E(\vec{F})}{\partial F_i \partial F_j} \right)_{\vec{F}=0}$$

where i and j stand for the cartesian coordinates. Useful quantities to characterize the electronic structure of clusters are the mean polarizability and its anisotropy which, using the diagonal components, are, respectively defined as:

$$\langle \alpha \rangle = \frac{1}{3} \text{tr}[\alpha] = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

and

$$|\Delta\alpha|^2 = \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2].$$

3. Results and discussion

Firstly, the discussion will be focused on the planar structures of $\text{Si}_{10}\text{Li}_8$ clusters in order to extend it to achieve the three-dimensional arrangements. In Table 1 are collected all data reported here, i.e. the relative energy computed at B3LYP/Def2-TZVP level, the

HOMO–LUMO gap, the bifurcation values of total and σ – π contributions of ELF for all planar structures, and the isotropic polarizability values for all systems.

3.1. Structural motifs

The planar structures previously reported for $\text{Si}_{10}\text{Li}_8$ clusters by Jing et al. [18] are shown in Figure 1. All structures present a common core formed by two six-membered silicon rings. As it has been proposed, the aromaticity plays a key role in their stability. It can be noted from the relative energy reported in Table 1 that D-1 is more stable than D-2 by 0.79 eV and D-2 than D-3 by 2.31 eV. This trend is presumably due to the fact that the out-of-plane Li atoms facilitate the delocalization of π -electrons in D-1 and D-2 comparing with D-3 motif. The main difference between D-1 and D-2 clusters is the bonding mode of the lithium atoms in the molecular plane, there are two bridge bond types, i.e. with alternate and adjacent silicon atoms in the former whereas only one bridge bond type (with adjacent atoms) in the latter, the alternate bond type can support the π -delocalization gained by the system.

We have also explored a new set of structural motifs which presents the core formed by two silicon rings nearly flat and two out-of-plane Li atoms bonded to it by only one side; the structures are labeled as D-4, D-5, D-6, and D-7 in Figure 2. Notice that these structure-types fall in the range of 1.88–2.59 eV, being less stable than D-1 and D-2 structures. The out-of-plane Li atoms by one side induce polarization of the electron density in distorted Si_{10} structures resulting in less stable isomers than structures with out-of-plane Li atoms in both sides.

In Figure 3 are shown the new motifs found for $\text{Si}_{10}\text{Li}_8$ by using starting structures localized by stochastic procedure [19] as mentioned in computational details, i.e. three-dimensional structures labeled as 3D-1 and 3D-2. Our results show that both structures have lower total energy than the planar ones, being 3D-1 more stable than D-1 by 0.47 eV. Notice that 3D-1 can be divided into three main molecular fragments: Si_2 , Li_4 , $\text{Si}_8\text{-Li}_4$. This structural motif presents some similarities to one previously reported for other lithium–silicon cluster (Si_6Li_6) by Santos et al. [17] where silicon dimer, lithium tetramer and $\text{Si}_4\text{-Li}_2$ fragments can be identified, which is characterized by a lower value of dielectric polarizability indicating that it is a more compact structure.

3.2. Electronic analysis: ELF and natural atomic charges

As can be seen from Table 1, the bifurcation values of total and σ – π contributions of ELF are quoted for all planar and quasi-planar structures. The bifurcation values of total ELF are in the range 0.68–0.75, which are quite closer to the reported value for naphthalene (used as the reference data, 0.76), [27] indicating that the aromaticity in the set of D-1 – D-7 structures is quite similar. On the other hand, the π contribution to the aromaticity is higher than

Table 1
Relative energies, HOMO–LUMO gap, total and σ – π ELF bifurcation values, polarizability and its anisotropy values for $\text{Si}_{10}\text{Li}_8$ isomers. These results were obtained at the B3LYP/Def2-TZVP level, the most stable structure is considered as the zero energy.

Systems	Relative energy (eV)	HOMO–LUMO gap (eV)	Total ELF	ELF- π	ELF- σ	Polarizability α (bohr ³)	$\Delta\alpha$
3D-1	0	2.64	–	–	–	498.0	190.2
3D-2	0.379	2.16	–	–	–	545.1	216.8
D-1	0.470	1.76	0.72	0.82	0.64	610.7	517.0
D-2	1.258	1.87	0.70	0.80	0.62	636.1	532.6
D-4	1.878	2.09	0.68	0.61	0.64	683.7	628.5
D-5	1.932	2.13	0.68	0.80	0.68	686.6	636.9
D-6	1.959	2.19	0.69	0.76	0.68	673.9	562.9
D-7	2.585	2.05	0.70	0.75	0.63	713.5	680.3
D-3	3.566	2.14	0.75	0.72	0.59	763.6	735.0

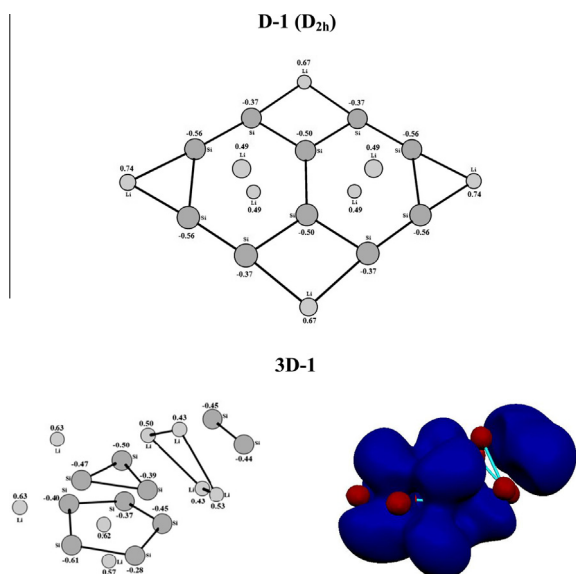


Figure 4. Natural atomic charge for the most stable two- (D-1) and three-dimensional structure (3D-1).

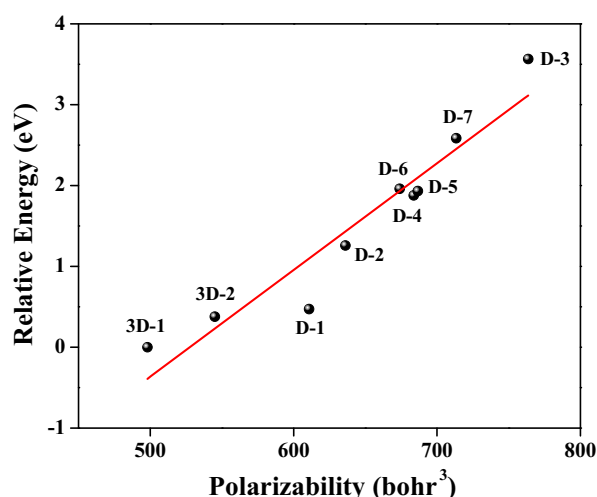


Figure 5. Relationship between the polarizability, α , and relative energy.

the σ one. However, any correlation between aromaticity and stability for planar and quasi-planar structures was not found.

Charge transfer from Li atoms to silicon fragment was obtained from natural population analysis as it is implemented in NBO program [38]. We have used the total charge transfer calculated as the sum of the atomic charge on Li atoms, the values are 4.76, 4.83, 4.86, 4.87, 4.88, 4.90 and 5.04|e| for planar and quasi-planar structures, D-1, D-2, D-4, D-5, D-6, D-7 and D-3, respectively, which are slightly reduced when structural transition to three-dimensional motif occurs, i.e., 4.35 and 4.40|e| for 3D-1 and 3D-2, respectively. Although an inverse relation between stability and total charge transfer can be seen, the latter fluctuates into a small range; therefore, it is not suitable to rationalize the stability order in $\text{Si}_{10}\text{Li}_8$ isomers. However, it is interesting to make some differences in the Li atom-types. In this sense, the ability to deplete electronic charge depends on the position of the Li atoms, i.e. out-of-plane or in the plane. Li atoms in the plane deplete more charge than those out-of-plane in two-dimensional motifs as displayed Figure 4. In consequence, the π -electron delocalization in silicon rings is reinforced by the higher electron charge released from Li atom in the molecular plane.

On the other hand, the atomic charges shown in Figure 4 help to rationalize the higher stability of 3D-1 isomer, it is driven by strong electrostatic interactions between Li_4 fragment with the other two, Si_2 and $\text{Si}_8\text{-Li}_4$. It can be noted that lithium tetramer (which is the central fragment) depletes 1.88|e|, while Si_2 and $\text{Si}_8\text{-Li}_4$ fragments accumulate 0.89|e| and 0.99|e|, respectively. This shows that the formation of the 3D-1 isomer can be seen as an electron transfer process given by the oxidation of lithium tetramer, at two electrons, with the consequent reduction of both fragments, i.e. Si_2 and $\text{Si}_8\text{-Li}_4$. For 3D-2 isomer a similar structure and analysis was done, here the fragments identified are Si_2 , Li_3 , and $\text{Si}_8\text{-Li}_5$. In summary, the through space or electrostatic interactions could be behind the stability in three-dimensional motifs.

3.3. HOMO–LUMO gap and polarizability

In Table 1, the HOMO–LUMO gap and polarizabilities for all isomers are also reported. The HOMO–LUMO gap is associated with the chemical hardness, a property related with stability. However, no correlation was found despite the most stable structure is the harder specie.

The polarizability values show that the three-dimensional structures have smaller polarizability and lower energy than planar ones, being 3D-1 the structure with the smallest polarizability value. Three-dimensional structure turned out to be more compact than the planar ones since they are mainly stabilized by electrostatic interactions. Thus, it is possible to state that more compact electronic structure leads to lower polarizability as well as its anisotropy. This statement could also explain the stability order between planar and quasi-planar with three-dimensional motifs. Notice that the polarizability values correlate in good order with the relative stability along the isomers studied. Thus, the minimum polarizability principle, which states that any system should proceed toward a state of minimum polarizability, is fulfilled. Finally, the above-mentioned result is shown in Figure 5 where a good linear relationship connecting the polarizability, α , with the relative energy of the cluster was found.

4. Concluding remarks

Exploration of the $\text{Si}_{10}\text{Li}_8$ potential energy surface by using starting structures resulting from stochastic procedure showed that the most stable isomer is a three-dimensional structure which is stabilized by electrostatic interactions between the three main fragments, $\text{Si}_2 \cdots \text{Li}_4 \cdots \text{Si}_8\text{Li}_4$; as it was supported by the natural atomic charge analysis. It was no trivial to establish a relationship between stability and aromaticity, which indicates that aromaticity is not the determining factor within the stability of $\text{Si}_{10}\text{Li}_8$ cluster. The minimum polarizability principle proposed by Chattaraj and Sengupta, was fulfilled, thus allowing to state that polarizability has a greater importance than other factors when it comes to establish the stability order, at least in the studied system.

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