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[n]Sila-acenes (n=2-4): The Influence of Ring Size on the Properties

Hossein Ghiasi, Reza Ghiasi*

Department of Chemistry, Basic Science Faculty, East Tehran Branch, Qiamdasht, Islamic Azad University, Tehran, IRAN

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Abstract

The structures and properties of [n]sila-acenes (n=2-4) were investigated by density functional theory method. The results of calculations were obtained at B3LYP/6-311G (d,p) level on model species. Energetic criteria suggest that **2-1b (n=2), 3-1b (n=3), and 4-1b (n=4)** isomers enjoy stabilization. By frontier orbital analysis, these systems are among the most stable of the family. Also, calculations indicate the most stable isomers have the most first hyperpolarizability values. The aromaticity of all molecules has been studied by nucleus-independent chemical shift..

Key words: *Sila-polyacenes, DFT calculations, Hyperpolarizability, Nucleus-independent chemical (NICS).*

Introduction

Polyacenes belong to a class of polycyclic aromatic hydrocarbon (PAH) compounds which are planar sets of linearly fused benzene rings with the general formula $C_{4n+2}H_{2n+4}$ or $C_2H_4(C_4H_2)m$. Much attentions have been paid to polyacene molecules [1], because of their role to form the basic cylindrical carbon units of single-wall nanotubes and possible utility of their cyclical cavities in host–guest phenomena [2, 3], therefore, resultant B–N analogues (cyclo BN-acene) as important applied materials in above mentioned fields, have attracted many experimental [2] and theoretical chemists[4-9]. Aromaticity in polyacene analogue of inorganic ring compounds (BN-acenes, CN-acenes, AlN-acenes, BO-acenes, BS-acenes, and Na6-acenes) has been investigated [10, 11]. The conceptual density functional theory-based reactivity descriptors and the nucleus-independent chemical shift (NICS) values in their calculations have been used in these studies.

***Corresponding author:** *Dr. Reza Ghiasi, Associate Prof., Department of Chemistry, Basic Science Faculty, East Tehran Branch, Qiamdasht, Islamic Azad University, Tehran, IRAN. E-mail: rghyasi@qdiau.ac.ir.*

In this research, the structural, electronic properties and aromaticity in a series of [n] sila-acenes with n=1-4 were analyzed using theoretical method

Computational methods

All calculations were carried out with the Gaussian 03 suite of program [12]. The calculations of systems contain C, Si, and H described by the standard 6-311G (d,p) basis set [13-16]. A vibrational analysis was performed at each stationary point conforms its identity as an energy minimum. The nucleus-independent chemical shift (NICS)is defined as the absolute magnetic shielding computed at the center of a ring in a molecule[17, 18]. NICS (0), NICS (0.5), NICS(1.0), NICS(1.5) and NICS(2.0) are calculated at the center and 0.5, 1.0, 1.5, and 2.0 Å above the ring, respectively. The electronic spectra for the studied compounds were calculated by TD-DFT [19] using the same hybrid functional and basis sets as used for the calculation of the hyper polarizabilities. The 10 lowest excitation energies were computed.

Geometries were optimized at this level of theory without any symmetry constraints followed by the calculations of the first order hyperpolarizabilities. The total static first hyper polarizability β was obtained from the relation:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

upon calculating the individual static components

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i\neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Due to the Kleinman symmetry [20]:

$$\beta_{xyy} = \beta_{yxy} = \beta_{yyx}\ ;\ \beta_{yyz} = \beta_{yzy} = \beta_{zyy}, \ldots$$

one finally obtains the equation that has been employed:

$$\beta_{tot} = [(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2]^{1/2}$$

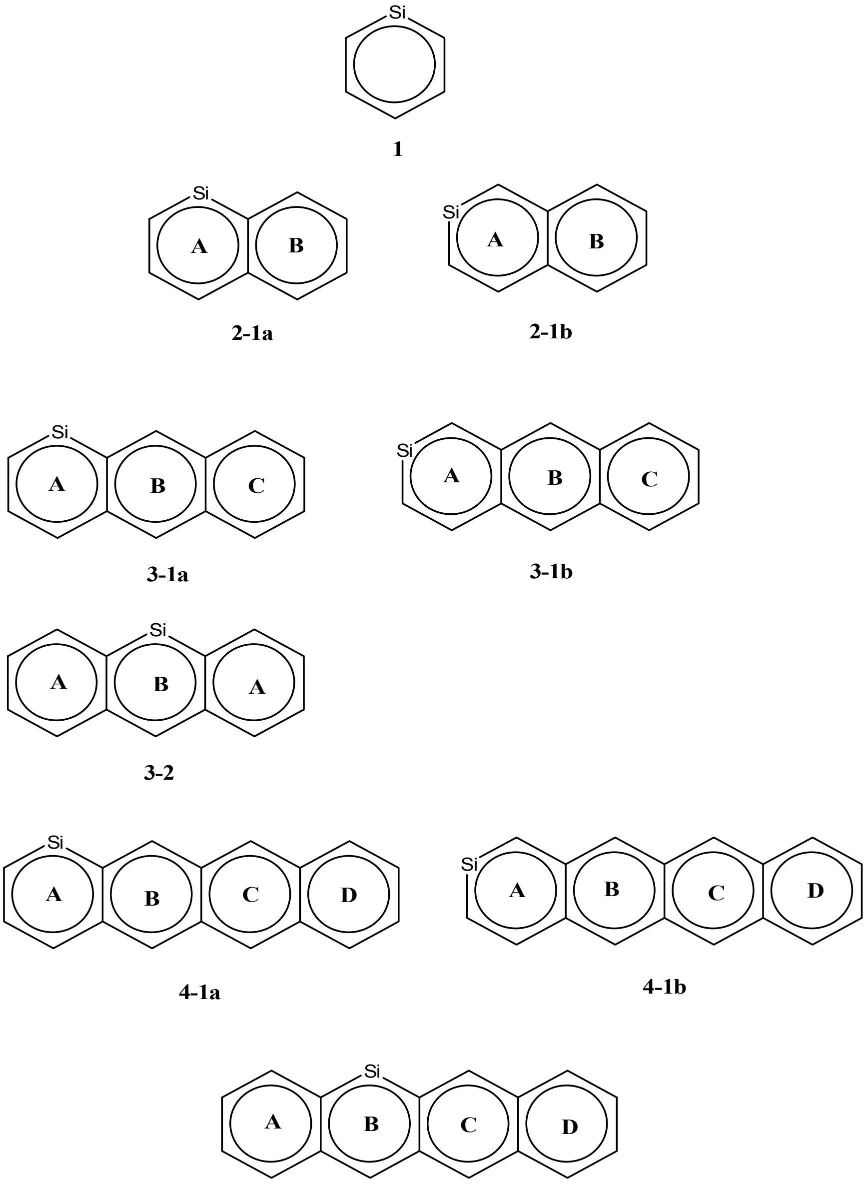
Results and discussion

Energetic aspects

Figure 1 shows the optimized geometries and structural parameters of all molecules. The equilibrium structures of all molecules are planar. The calculated relative energy (ΔE), polarizability (α), HOMO-LUMO gaps are listed in Tables 1-2. When the compounds are classified with geometric isomers, **2-1a, 3-1b** and **4-1b** are energetically more stable, and harder than the other isomers. As expected from the principles of minimum energy, minimum polarizability, and maximum HOMO-LUMO gaps, that is, when an isomer changes from the most stable to other less stable species in most cases, the energy increases, and the HOMO-LUMO gaps decreases (Table 2).

Table1 . Calculated Energy (Hartree), relative energy (kcal/mol), Dipole moment (μ, Debye), Isotropic <α> and anisotropic (Δα) polarizability for sila-polyacenesby the method B3LYP with 6-311G (d,p) basis set.

Molecule	E(Hartree)	ΔE	μ	<α>	Δα
1	-483.671	0.00	0.3563	77.75	39.27
2-1a	-637.346	0.30	0.5863	126.51	77.15
2-1b	-637.346	0.00	0.5589	128.84	84.62
3-1a	-791.016	0.32	0.7831	186.90	127.66
3-1b	-791.017	0.00	0.7473	192.43	132.34
3-2	-791.015	1.43	0.5845	187.15	143.16
4-1a	-944.684	0.45	0.9209	258.75	210.28
4-1b	-944.685	0.00	0.9063	268.02	225.92
4-2	-944.683	1.08	0.7153	259.22	224.55



1

2-1a **2-1b**

3-1a **3-1b**

3-2

4-1a **4-1b**

4-2

Figure 1. Geometries of sila-polyacenes.

Table 2. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), Hardness (eV), chemical potential (eV), and electrophilicity (eV) for sila-polyacenesby the method B3LYP with 6-311G(d,p) basis set.

Molecule	HOMO	LUMO	ΔE	η	S	μ	ω
1	-0.218	-0.035	4.97	2.49	0.20	-3.45	2.39
2-1a	-0.200	-0.056	3.92	1.96	0.26	-3.47	3.08
2-1b	-0.206	-0.053	4.15	2.08	0.24	-3.53	3.01
3-1a	-0.189	-0.074	3.12	1.56	0.32	-3.58	4.11
3-1b	-0.192	-0.072	3.27	1.63	0.31	-3.61	3.98
3-2	-0.181	-0.073	2.95	1.47	0.34	-3.47	4.08
4-1a	-0.181	-0.089	2.52	1.26	0.40	-3.67	5.36
4-1b	-0.182	-0.086	2.60	1.30	0.38	-3.65	5.13
4-2	-0.173	-0.087	2.34	1.17	0.43	-3.53	5.32

Polarizability

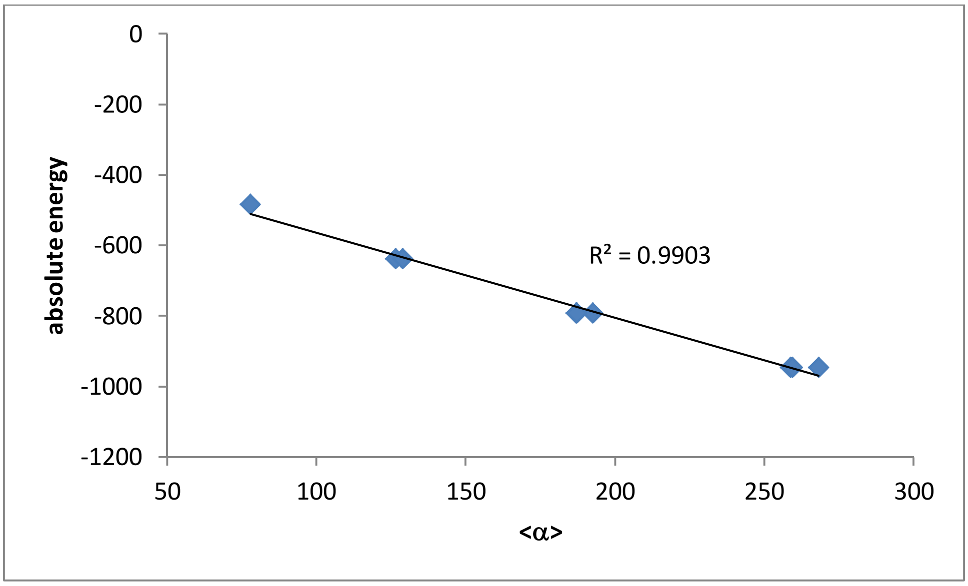
Polarizability describes the response of a system in an applied electric field [21]. They determine not only the strength of molecular interactions (such as the long range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties of the system [22]. The isotropic polarizability<α> is calculated as the mean value as given in the following equation[23]:

$$\langle\alpha\rangle = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3}$$

And the polarizability anisotropy invariant is

$$\Delta\alpha = \left[\frac{(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 + (\alpha_{ZZ} - \alpha_{XX})^2}{2}\right]^{\frac{1}{2}}$$

Calculations show increasing of these values with increasing number of ring (Table 1). On the other hand, there is a good correlation between these values with absolute energy values (Figure 2).



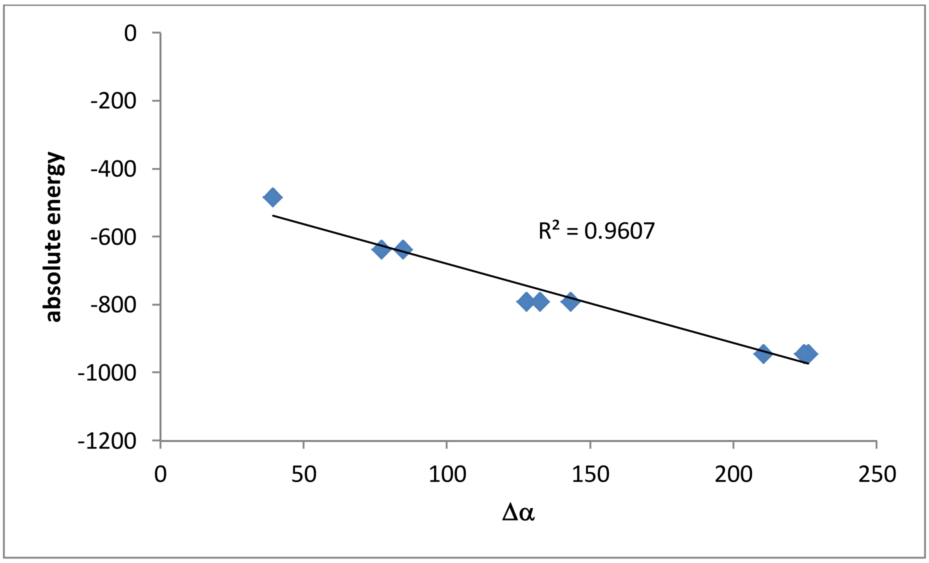


Figure 2. A linear correlation between absolute energy with isotropic and anisotropic polarizability values in sila-polyacenes.

Frontier orbital energies and chemical hardness

The frontier orbital energies, HOMO-LUMO gap energy, hardness, chemical potential, and electrophilicity of all molecules computed are given in the Table 2. These values indicate the energy of the frontier orbitals is less in the complexes.

To evaluate the hardness and chemical potential of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expression:

$$\mu=(\varepsilon_{HOMO}+\varepsilon_{LUMO})/2$$

$$\eta=(\varepsilon_{HOMO}-\varepsilon_{LUMO})/2$$

Where μ is the chemical potential (the negative of the electronegativity), and η is the hardness [24, 25]. The hardness values decrease with the increasing of the rings (Table 2).

To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index,ω, for each complex measured according to Parr, Szentpaly, and Liu [26] using the expression:

$$\omega=\frac{\mu^2}{2\eta}$$

The values of electrophilicity index in Table 2 increase with the increasing of the rings.

There is a linear correlation between <α> and Δα values with HOMO-LUMO gaps energies (Figure 3).

Figure 4 confirms the linear behavior between $\alpha^{1/3}$ and 2S, where S is the softness, given by 1/(2η), as expected [27].

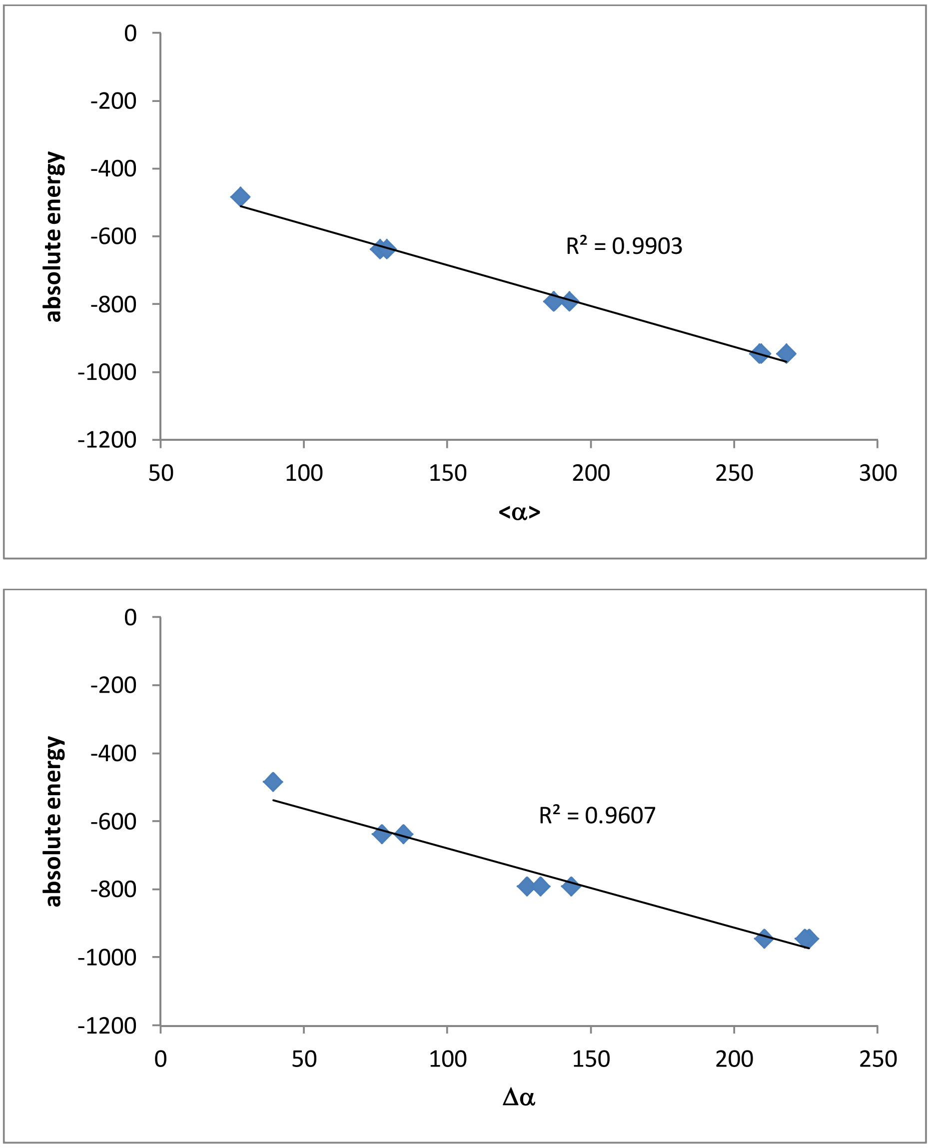


Figure 2. A linear correlation between absolute energy with isotropic and anisotropic polarizability values in sila-polyacenes.

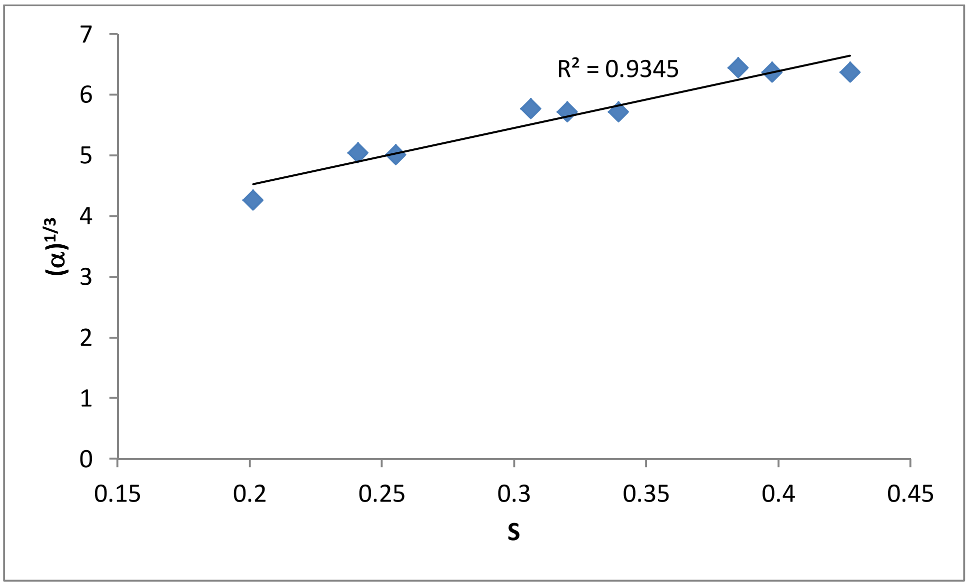


Figure 4. A linear correlation betweensoftness and <α>$^{1/3}$ values in sila-polyacenes.

Nucleus Independent Chemical Shift analyses (NICS)

NICS is an easy and efficient criterion to identify aromatic nature. A large negative NICS at the ring center (or inside and above the molecular plane) implies the presence of diamagnetic ring currents. As shown in Table 3, all the computed NICS (0.0) values at the geometrical center of cycles are negative, suggesting that such frames are obviously aromatic. In order to further identify the aromaticity of the molecules, we calculated the NICS values (including NICS (0.5), NICS(1.0), NICS(1.5), and NICS(2.0)) by placing a series of ghost atoms above (by 0.5, 1.0, 1.5, 2.0 Å) the geometrical centers. All these NICS values are mainly attribute to the delocalized π electrons current. They are shown in Table 3in detail and are all negative. Although the negative sings for NICS of the rings suggest those molecules to be aromatic. These values show that as the distance in vertical direction increases, the NICS values firstly change little and then decrease gradually. The negative values inside and above the rings adequately prove that the diamagnetic ring current effect, characteristic for aromaticity, exists in these ground states. Average of NICS values for molecules shows increasing of aromaticity with the increasing of rings. There is a linear correlation between $<\text{NICS (1.0)}>_{\text{molecule}}$ values and n (Figure 5).

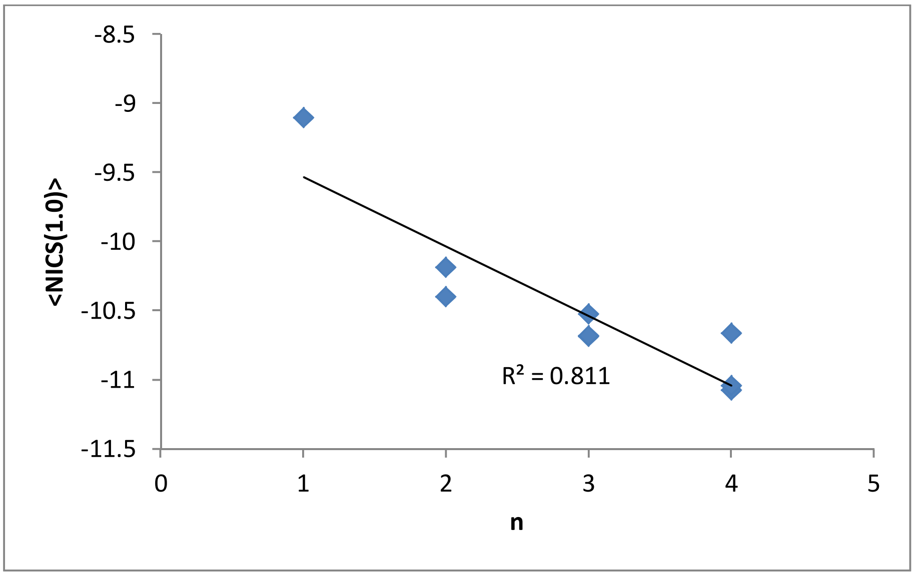


Figure 5. A linear correlation between<NICS(1.0)>$_{molecule}$ and n values in sila-polyacenes.

Table 3. NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5), and NICS(2.0) values for sila-polyacenes by the method B3LYP with 6-311G(d,p) basis set.

Molecule	ring	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
1	**A**	-8.34	-9.19	-9.10	-7.06	-4.74
2-1a	**A**	-8.70	-9.60	-9.41	-7.28	-4.98
	B	-8.59	-10.59	-10.95	-8.19	-5.34
2-1b	**A**	-9.14	-10.02	-9.77	-7.49	-5.08
	B	-8.95	-10.81	-11.03	-8.25	-5.40
3-1a	**A**	-6.97	-7.99	-8.19	-6.53	-4.61
	B	-11.37	-13.41	-13.27	-9.79	-6.47
	C	-8.20	-10.15	-10.60	-8.03	-5.34
3-1b	**A**	-7.06	-8.20	-8.44	-6.69	-4.69
	B	-11.40	-13.33	-13.20	-9.78	-6.47
	C	-7.92	-9.87	-10.40	-7.90	-5.24
3-2	**A**	-7.41	-9.33	-9.84	-7.44	-4.90
	B	-10.49	-11.46	-11.21	-8.70	-6.03
4-1a	**A**	-6.34	-7.25	-7.48	-6.00	-4.24
	B	-11.62	-13.67	-13.36	-9.80	-6.50
	C	-12.01	-14.01	-13.80	-10.24	-6.84
	D	-7.02	-8.97	-9.66	-7.44	-4.99
4-1b	**A**	-6.57	-7.54	-7.74	-6.11	-4.25
	B	-11.30	-13.25	-13.12	-9.74	-6.49
	C	-11.87	-13.88	-13.64	-10.09	-6.72
	D	-7.20	-9.12	-9.67	-7.40	-4.96
4-2	**A**	-6.37	-8.26	-8.92	-6.81	-4.52
	B	-10.01	-11.08	-10.98	-8.62	-6.04
	C	-10.95	-12.98	-12.97	-9.65	-6.42
	D	-7.26	-9.21	-9.77	-7.42	-4.91

Electronic spectra

We found the most intense electronic transition (λ_{max}) of molecules. The wavelength, oscillator strength and the composition of the transitions obtained by TD-DFT calculations are given in Table 4. There is a good correlation between β_{tot} and λ_{max} (Figure 6). The most intense electronic transition is attributed to HOMO-1→LUMO transition (n=2, 3: **3-1b** and **3-2** isomers) and for n=4 and 3-1a isomer is HOMO-2→LUMO.

Table 4. Maximum Absorption wavelength (λ_{max}), and Oscillator strength (f) for sila-polyacenesby the method B3LYP with 6-311G(d,p) basis set.

Molecule	character	λ_{max}	f	$\beta_{tot}\times10^{-30}$
1	HOMO-1 → LUMO	200.36	0.3239	1.77
2-1a	HOMO-1 → LUMO	230.07	0.5409	2.15
2-1b	HOMO-1 → LUMO	250.67	0.4915	3.87
3-1a	HOMO-2 → LUMO	259.18	0.9934	3.46
3-1b	HOMO-1 → LUMO	281.79	0.7647	5.72
3-2	HOMO-1 → LUMO	255.03	1.4069	2.69
4-1a	HOMO-2 → LUMO	280.52	0.8391	4.88
4-1b	HOMO-2 → LUMO	284.93	1.2351	5.59
4-2	HOMO-2 → LUMO	282.35	1.7871	4.80

Hyper polarizability

The first static hyper polarizability (β_{tot}) values for the all molecules are shown in Table 5. The results show that the magnitude of the first hyper polarizability tensor of all molecules is rather moderate. These values indicate the most stable isomer has the most first hyper polarizability.

A good correlation between β_{tot} and λ_{max} suggested that this transition participate a significant role in determining β (Figure 6).

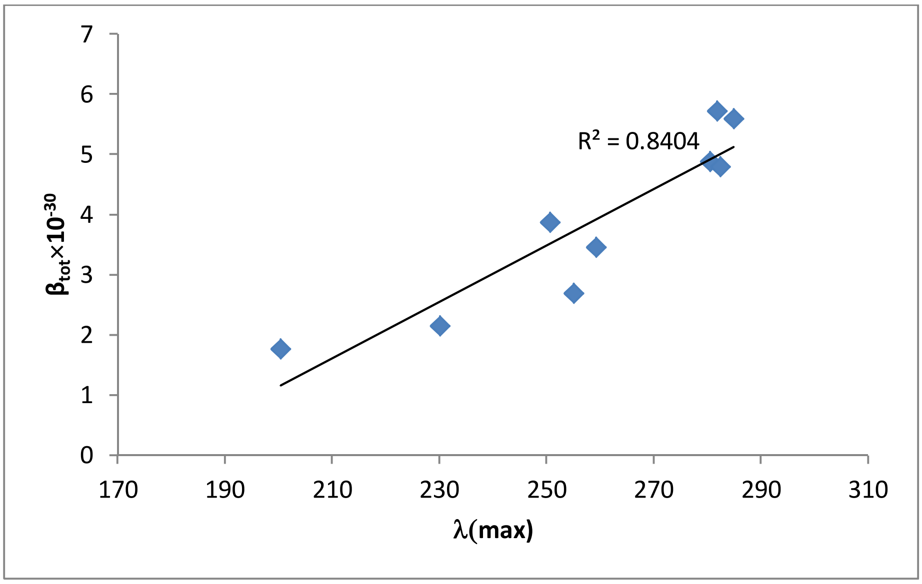


Figure 6. A linear correlation betweenλ_{max} and hyperpolarizability values in sila-polyacenes.

Table 5. βcomponents & β_{tot} values (10^{-30}esu) for sila-polyacenesby the method B3LYP with 6-311G(d,p) basis set.

Molecule	1	2-1a	2-1b	3-1a	3-1b	3-2	4-1a	4-1b	4-2
β_{XXX}	64.64	-139.75	295.23	-353.10	456.03	-1.52	-418.39	-640.00	423.02
β_{XXY}	58.90	-4.68	1.77	3.04	-2.31	-0.12	-2.69	-2.20	-0.51
β_{XYY}	22.44	34.41	134.08	60.20	173.44	-0.61	50.67	70.02	-18.83
β_{YYY}	-7.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
β_{XXZ}	-0.13	-1.03	38.58	18.60	-10.61	12.81	126.60	-25.44	6.24
β_{XYZ}	0.13	0.91	2.78	2.90	-4.14	3.69	1.08	-1.25	4.31
β_{YYZ}	0.19	111.84	39.94	115.21	29.60	117.89	66.31	112.23	133.02
β_{XZZ}	89.87	32.21	18.20	14.66	27.75	-6.60	-125.83	-22.99	31.22
β_{YZZ}	51.89	0.36	0.16	-2.81	-5.59	10.69	-0.21	-1.17	-5.18
β_{ZZZ}	0.00	126.73	-60.84	154.48	-101.37	179.80	81.90	172.47	206.29
β_{tot}	1.77E-30	2.15E-30	3.87E-30	3.46E-30	5.72E-30	2.69E-30	4.88E-30	5.59E-30	4.80E-30
$\beta_{tot}\times10^{-30}$	1.77	2.15	3.87	3.46	5.72	2.69	4.88	5.59	4.80

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