

# Theoretical study of polaron binding energy in conformationally disrupted oligosilanes

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**Abstract** Density functional theory was used for a quantum chemical study of oligo[methyl(phenyl)silylene] structures containing a conformational defect: a kink in the silicon backbone. Oligomers were studied in the neutral state as well as in the form of positive ( $P^+$ ) and negative ( $P^-$ ) polaron quasiparticles. Computations performed using the B3LYP model and the 6-31G(d) basis set revealed that the charge distribution is not influenced by the presence of the kink, but the positive charge on the Si backbone differs slightly in  $P^+$  and  $P^-$  quasiparticles. On the other hand, the spin density is significantly shifted away from the chain part that contains the kink, and this effect is more intense in  $P^-$  polarons. Changes in electron density are also evident from the frontier molecular orbital distribution. The deformation energy (which is associated with the relaxation of polarons) decreases with the number of atoms in the oligomer backbone in  $P^+$  but shows the opposite behavior for  $P^-$  quasiparticles.

**Keywords** Oligo[methyl(phenyl)silylene] · Polaron · Spin density · Charge · Density functional theory

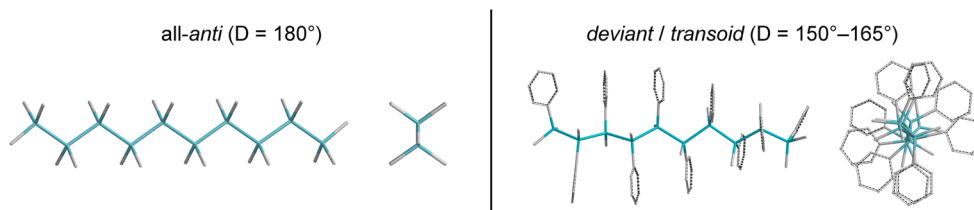
## Introduction

Polymers that contain silicon (Si) atoms as the structural units in their backbones show remarkable and unique electron properties. Electrons are delocalized along the chain since the vicinal and geminal Si orbitals overlap, enabling the formation of a continuous space that can be occupied by  $\sigma$

electrons. This  $\sigma$  conjugation is similar and often compared to  $\pi$  conjugation in compounds with carbon backbones, even though they have different origins [1–3]. Poly[methyl(phenyl)silylene] (PMPSi) is a commonly studied polymer of this type because it is attainable, processable, and presents both  $\sigma$  and  $\pi$  bonds on the backbone and aromatic substituent, respectively. Further, PMPSi is a semicrystalline polymer with properties that are influenced by both the backbone conformation and the presence of substituents [4]. Generally, the conformations of polysilylenes are described by the values of dihedral angles, each of which is defined by the relative positions of four successive silicon atoms [5]. The ideal conformation is all-*anti*, meaning that the silicon chain is stretched, all dihedral angles are equal to  $180^\circ$ , electrons are regularly delocalized, and  $\sigma$  conjugation is maximized [6]. However, the presence of a bulky substituent such as a phenyl group discourages this arrangement, leading to the formation of a left- or right-handed helix structure with dihedral angles close to the *deviant* ( $150^\circ$ ) or *transoid* ( $165^\circ$ ) conformation [7, 8]. The difference between these two conformations is depicted visually in Fig. 1.

Some backbone deformations or defects, such as bends in the chains and disruptions to the ideal conformation, can appear in the chains. As would be expected, such backbone defects influence the properties of the polymer that are related to electron delocalization, such as the absorption maximum ( $\lambda_{\max}$ ) or the course of the excitation process itself, since it can disrupt the overlaps between orbitals. We performed a theoretical investigation of such a defect—a kink consisting of four silicon atoms in an approximately *gauche* conformation, which was introduced into oligo[methyl(phenyl)silylene] chains—in our previous work [9]. It was discovered that  $\lambda_{\max}$  shifted to shorter wavelengths as the position of the kink was moved towards the center of the oligomer. Moreover, when the chain was divided into a longer and a shorter part by the

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**Fig. 1** Ideal deca(dimethylsilylene) (all-*anti*) and real deca[(methyl)phenylsilylene] (*deviant/transoid*) conformations of a decasilane chain ( $D$  dihedral angles in the silicon backbone)

kink, the frontier molecular orbitals were delocalized more on the longer part of the chain.

Another deeply investigated area of poly/oligosilylene molecules is their ability to form polaron quasiparticles. A polaron quasiparticle is a relaxed system with either a positive or a negative excess charge. It can be considered a (macro)molecule that alters the positions of its atoms in order to minimize its potential energy when a charge carrier is present [10]. Theoretical research in this field (primarily on equilibrium geometries, charge distributions, and polaron binding energies) is described in [10–15]. Si–Si bonds in both positive and negative polaron quasiparticles are longer than those found in the neutral geometry. Bond angles are smaller, and dihedral angles are similar in positive polarons and neutral molecules [10]. On the other hand, the bond angles are stretched in negatively charged polarons [11]. In addition, excess charge is accumulated on the attached substituents, whereas the spin density is greatest on the backbone [10–14]. Changes in energy between neutral and charged states of a molecule can be expressed via the polaron binding energy  $E_p$ , which consists of a deformation energy part and an electron–photon energy part. The former represents, on average, 90 % of the  $E_p$  of a polymer molecule, because the process of relaxation involves a significant change in the macromolecular conformation (i.e., shifts in the equilibrium positions of the atoms). The latter is obtained from the difference in the vibrational frequencies of the neutral molecule and the relaxed molecule [10]. Experimentally,  $E_p$  is found to have a value of 0.29 eV [16–19], which is in good agreement with theoretically calculated values, which are 0.20 eV on average [12]. All of these results were obtained from theoretical studies of oligomer-sized chains in the all-*anti* conformation. However, there were no reported studies of molecules with both a chain defect (a kink) and a polaron, so the present paper investigates such systems. Even though the all-*anti* conformation is an ideal case, kinks are conformational defects that are responsible for polymer chain folding or coil formation in real materials.

Therefore, the aim of the work reported in this paper was to describe the influence of a kink in an oligo[methyl(phenyl)silylene] chain in the form of a positive ( $P^+$ ) or a negative ( $P^-$ ) polaron quasiparticle. Equilibrium geometries, spin densities, charges, and deformation energies were investigated using density functional theory (DFT) and

the B3LYP hybrid model with the 6-31G(d) basis set. This level of theory and this model were chosen because they have already been successfully employed to perform calculations similar to those of interest to us in the present work (see, for instance, [10–13, 20]).

### Computational methods

Oligo[methyl(phenyl)silylene] (OMPSi $_n$ ) molecules were investigated via quantum chemical calculations performed in the Spartan '08 software (Wavefunction, Inc., Irvine, CA, USA) [21]. Oligomers ranging from two to ten repeated units in length were studied by DFT with the B3LYP (Becke–3-parameter–Lee–Yang–Parr) hybrid model and the 6-31G(d) basis set. Each end of the Si backbone was capped with a methyl group, and no geometric constraints were placed on the calculation. The molecules were treated as isolated in a vacuum environment.

Each molecule of OMPSi $_n$  was optimized with the theory described above. Structures of approximately *transoid* conformation were attained in the first step of the calculation. Afterwards, a set of semi-empirical PM3 calculations was performed to obtain energy profiles of the oligosilane conformers ( $n \geq 4$ ) with different values of the dihedral angle representing the kink which, in the ideal case, adopts the *syn* ( $0^\circ$ ) conformation. Using a plot of energy against dihedral angle, the most suitable conformers containing the kink were chosen and set as initial guesses for another structural optimization by DFT/B3LYP 6-31G(d) in order to obtain a new energy minimum, as well as to establish the geometry of the required kink more precisely. To ensure that the most appropriate results were obtained (i.e., to get the smallest kink angle possible and the true potential energy minimum), several geometry optimizations were run for each oligomer from different initial values of the kink angle. After optimization, this dihedral angle was measured virtually, which yielded values of  $50\text{--}60^\circ$  for all oligosilylenes, i.e., a kink with an approximately *gauche* conformation was formed.

Further, positive and negative polaron quasiparticles were created from the optimized structures in the cationic or anionic state, respectively. Firstly, the calculations were performed using the single point energy to obtain the oligomer [10] in the hot (i.e., unrelaxed) state. Finally, the polaron geometry

was optimized, which led to the formation of the relaxed structure. The unrestricted B3LYP model was used for these calculations, as it is suitable for open-shell systems. All other settings were kept the same.

## Results and discussion

### Geometry

The results of geometry optimization of neutral oligomers by DFT B3LYP/6-31G(d) are depicted in Fig. 2. As can be seen, the oligomer chain can adopt several conformations that differ in the position of the kink. Ten Si atoms in the chain enable the creation of four different structures with a kink. The number of potential kink positions is dependent on the number of silicon atoms in the backbone. For oligomers containing four or more units, the number of possible kink positions increases by one every two monomers added to the backbone. Figure 2 also provides information about the designation of the kink location in oligomers. The value (10) represents the size of the oligomer and the letter (A) shows where the first atom of the kink is located.

The dihedral angle for the kink was measured for each oligomer. The average value was  $54.7^\circ$ , irrespective of the direction in which the angle was measured. This angle increased during positive polaron ( $P^+$ ) formation to  $69.0^\circ$  but remained unchanged during negative quasiparticle ( $P^-$ ) formation ( $54.7^\circ$  on average).

Our investigation of the Si–Si bonds revealed (see Fig. 3) that these bonds lengthened during polaron relaxation. This effect was slightly more intense for  $P^+$  than for  $P^-$ . The longest bonds in molecules without the kink were found in the central part of the structure for all neutral ( $P^0$ ),  $P^+$ , and  $P^-$  oligomers. Another interesting fact can be ascertained from the lengths of the kink bonds. Each kink contains three bonds that are inconsistent in length when compared with the defectless

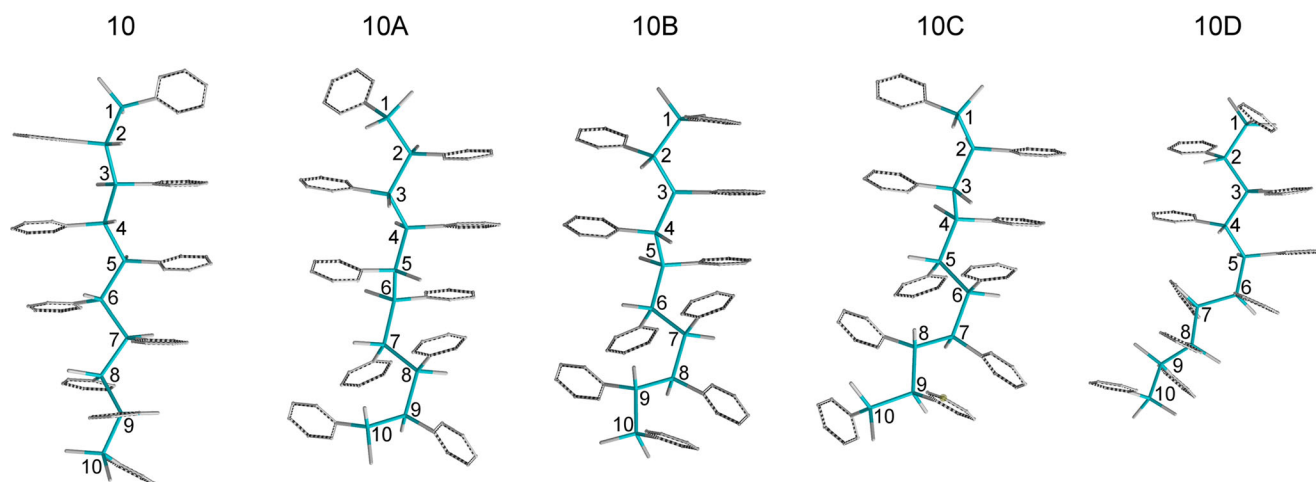
chain. The next adjacent bond right after the kink shows the longest length, which is significantly above average. The exception to this rule is the **10D** oligomer, where the longest bond is part of the kink. Similar trends can be observed for both the  $P^+$  and  $P^-$  structures.

A comparison of the bond lengths in other investigated  $OMPSi_n$  also revealed that the changes in bond lengths are greater in very short chains (2–4 units long). This may be due to the fact that atoms in short chains are less limited by the presence of other atoms and functional groups.

Bond angles are shown in Fig. 4. The angles in a defectless  $P^-$  decamer chain are about  $7^\circ$  higher than those in the neutral form, and they are highest in the central part of the backbone. Negative polarons are therefore more open structures. On the contrary,  $P^+$  structures without the kink have angles that are  $5^\circ$  smaller and the largest angles occur at the edges of the chain (as in the neutral case). These results are in agreement with those reported in the literature, as described in the “Introduction.” The insertion of a kink, however, caused the bond angles to change again. As can be seen in **10A–10D** of  $P^0$  and  $P^+$ , the largest bond angle is reached at the location of the kink. More precisely, the largest bond angle is the first angle in **10A–10C** and the second angle in **10D**, as the kink consists of two angles. This suggests that the part containing the defect stretches more than the rest of the chain, the angles of which are closer to those seen in the defectless chain. The situation is more complicated in  $P^-$ , as the highest angles are located furthest from the kink. Therefore, the part of the chain that is close to the kink contracts, as the angles are smaller than in the defectless chain. On the other hand, the remainder of the backbone is significantly stretched, as the angles are higher than in the no-kink chain.

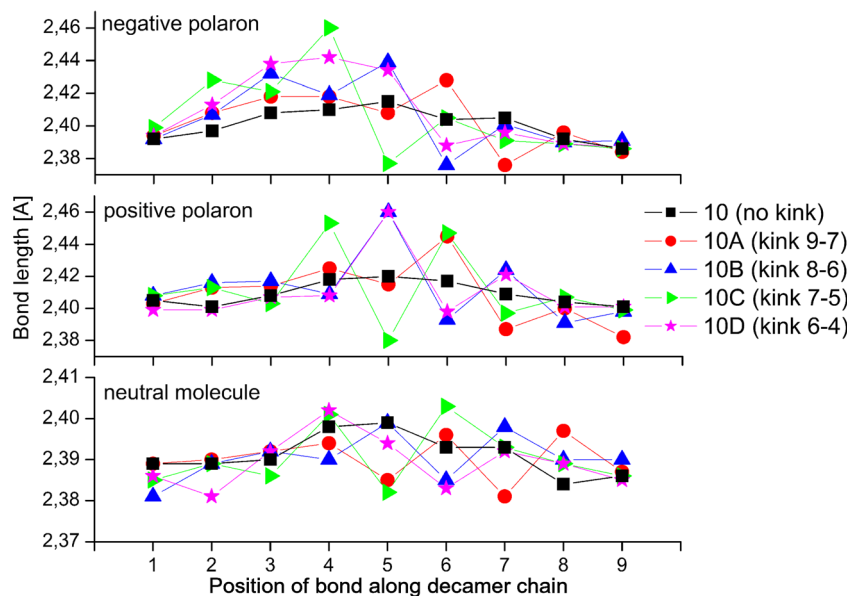
### Charge and spin distribution

Other monitored properties of oligosilanes are connected to the electron density distribution before and after polaron



**Fig. 2** Optimized structures (DFT B3LYP/6-31G(d)) of  $OMPSi_{10}$ , with atom numbering and molecule designation shown (H atoms are omitted)

**Fig. 3** Bond lengths (Si–Si) in the decamer chain, as calculated with DFT B3LYP/6-31G(d)

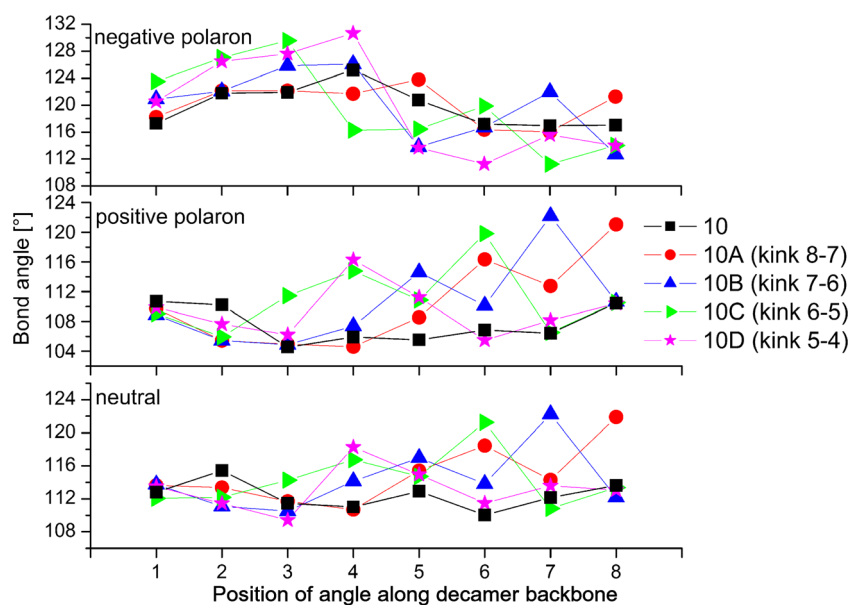


formation. Figure 5 shows the distribution of natural charge along the backbone of the decamer. The results for the  $P^0$ ,  $P^+$ , and  $P^-$  molecular states are displayed and compared. All Si chains are positively charged, with the highest charges seen on the edge atoms. This is probably due to Coulomb repulsion, which pushes the positive charge to the edges. The  $P^+$  state carries more charge, approximately  $0.05 e$ , than the neutral structure. If marginal atoms are not considered, the central part of the  $P^+$  decamer is the area with the highest charge. On the other hand, the  $P^-$  decamer carries a slightly lower charge (average difference  $0.05 e$ ) than the neutral molecule. Again, the lowest charge can be found at the center of the decamer. Figure 5 also presents a similar plot for carbon atoms from the methyl group and phenyl ring. The group of carbon atoms

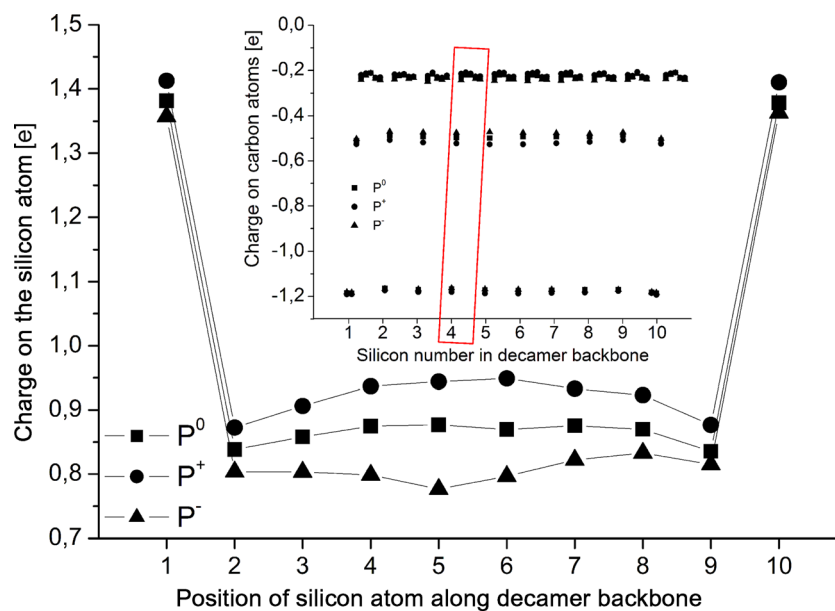
attached to a particular silicon atom (Si number 4 for example) is indicated by a rectangle. Methyl carbons carry a negative charge of around  $-1.17 e$ , carbons that link the Si chain to the phenyl have a charge of  $-0.48 e$ , and other carbons in the phenyl ring carry a charge of  $-0.23 e$ . The charges on structures containing the kink were compared with these curves, and their dependencies are shown in Fig. 6. However, this did not lead to any new insight as the differences between particular molecules are very slight. Therefore, it can be said that the kink does not cause any significant change in the charge distribution.

Figure 7 shows the spin distribution along the decamer backbone. The left graph shows the spin distributions for  $P^+$  quasiparticles and the right graph shows the distributions for

**Fig. 4** Bond angles (Si–Si–Si) in the decamer chain, as calculated with DFT B3LYP/6-31G(d)



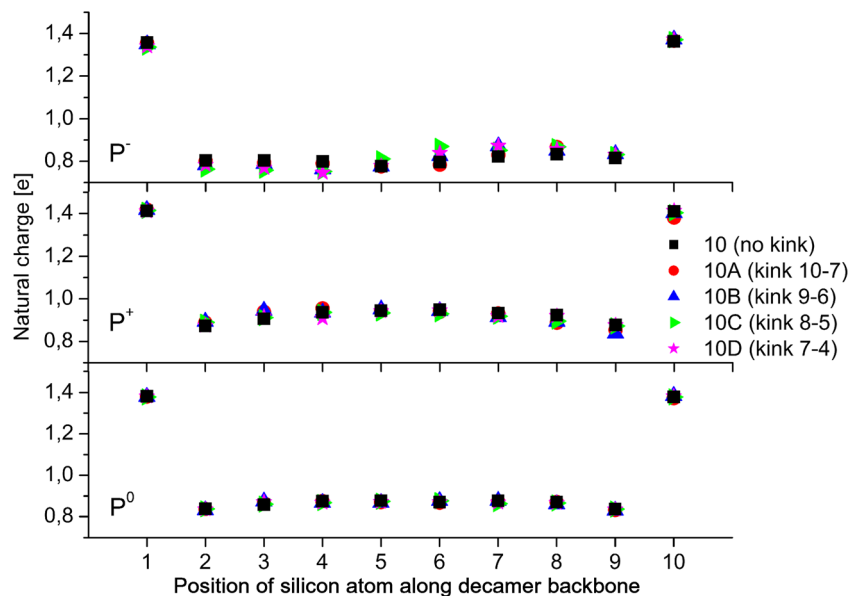
**Fig. 5** Natural charge distribution along the silicon chain and on the carbon atoms in decamer **10**, as calculated with DFT B3LYP/6-31G(d)

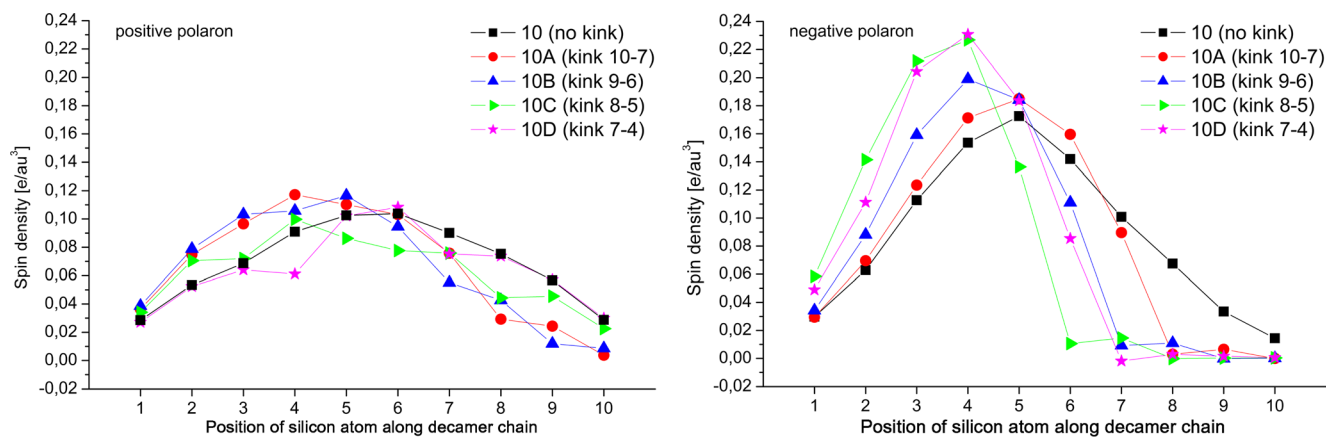


$P^-$  quasiparticles. In both of the defectless cases, the highest spin density is located in the central part of the backbone, which is in agreement with [11]. At the same time, the difference between the spin densities for  $P^-$  and  $P^+$  is about  $0.07 e/\text{au}^3$  at most. Further, introducing a kink significantly influences the spin density distribution. As can be observed in the plots for **10A–10D**, the spin density changes when the position of the kink in the chain is altered. The  $\sigma$ -orbital conjugation is disrupted by this conformational anomaly, which is displayed in the form of Kohn–Sham orbitals in Fig. 8. Therefore, the spin density is shifted away from the kink region to the regular parts of the oligomers, where it reaches its maximum.

As mentioned above and depicted in Fig. 8, the presence of a defect in the chain (the kink as well as the polaron) impacts on the delocalization of the HOMO (the highest occupied molecular orbital) and the LUMO (the lowest unoccupied molecular orbital). In neutral molecules (such as **10**), the HOMO and LUMO are regularly delocalized along the whole Si backbone. When the kink is introduced and the chain is divided by its presence into longer and shorter parts, the HOMO shifts to the longer part of the backbone. At the same time, the more symmetrical the division of the backbone by the kink, the more regularly the HOMO is delocalized. The LUMOs are concentrated in the central parts of the oligosilane chains on silicon atoms as well as on three adjacent phenyl

**Fig. 6** Natural charge along the Si backbone for all decamer structures in  $P^0$ ,  $P^+$ , and  $P^-$  form, as calculated with DFT B3LYP/6-31G(d)



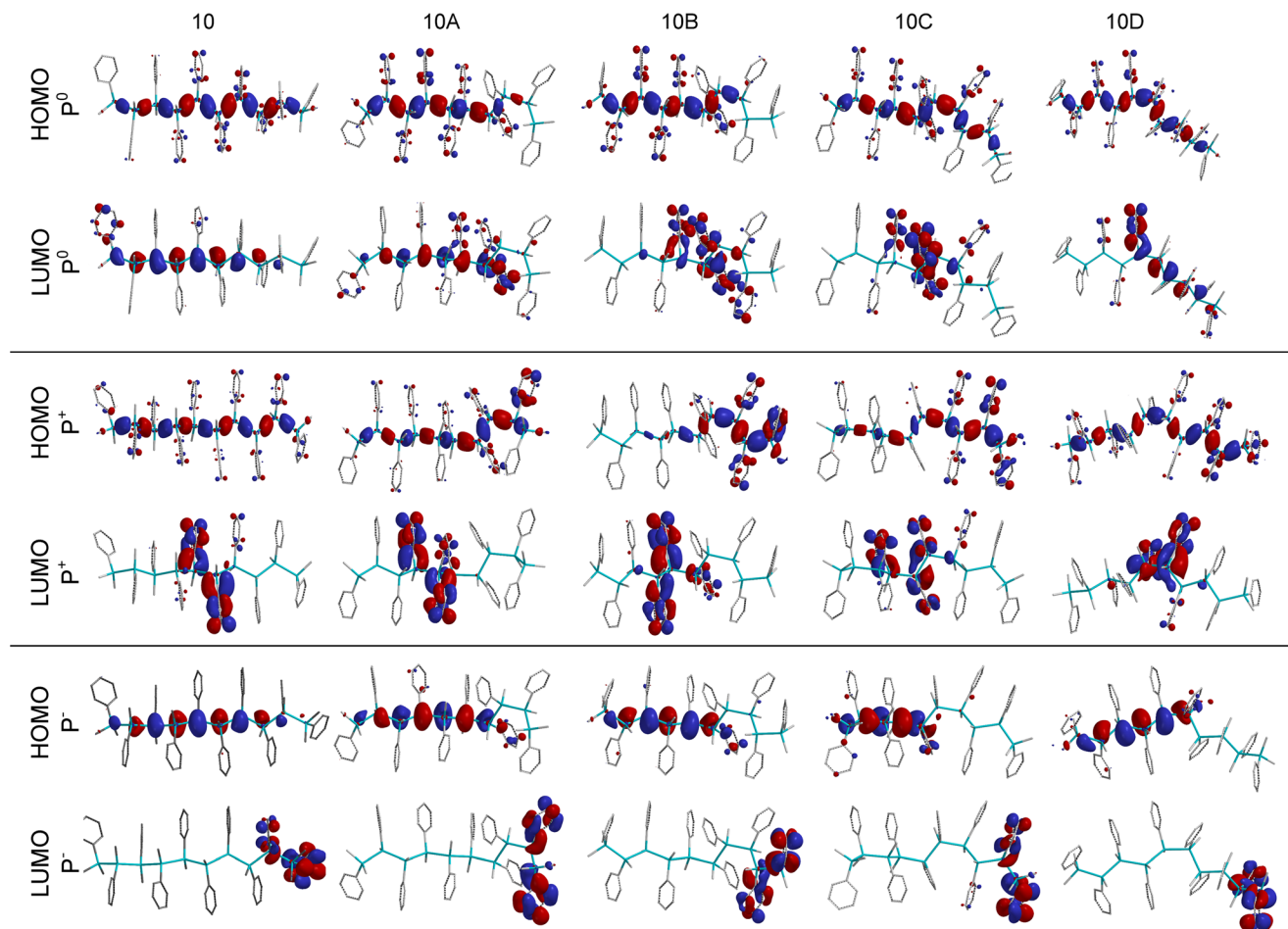


**Fig. 7** Spin distribution along the silicon decamer chain, as calculated with DFT B3LYP/6-31G (d). *Left panel:* positive polaron structures. *Right panel:* negative polaron structures

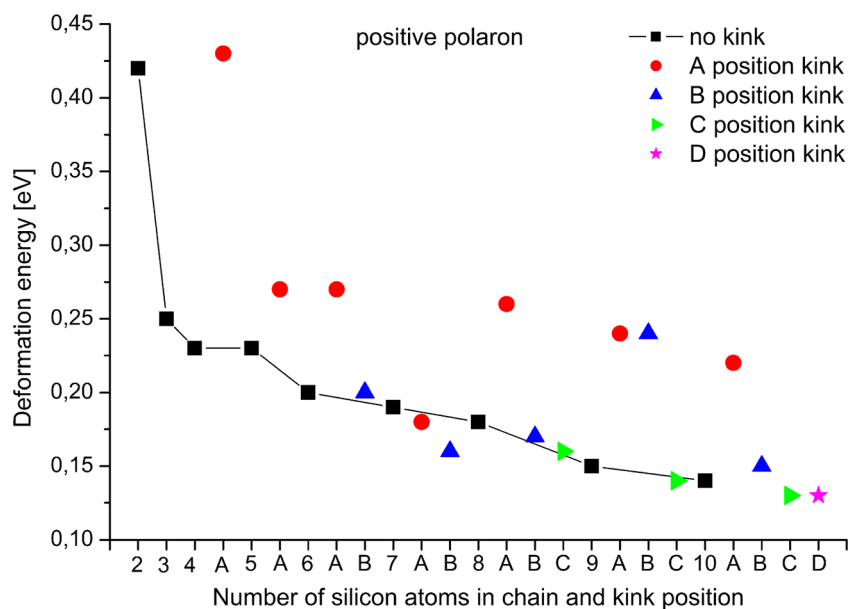
rings.  $P^+$  quasiparticles show a similar trend in the HOMO distribution to that seen for neutral molecules. However, they differ in the delocalization of the HOMOs, which are also present on the phenyl rings that are close to the kink. The LUMOs are only distributed in the center of

the chain on two or three phenyl rings that are attached to Si numbers 4, 5, and 6.

Finally, the HOMOs of negative polaron molecules alter considerably when a kink is inserted. These orbitals are delocalized on the Si atoms and they are located on the longer



**Fig. 8** Frontier molecular orbital (HOMO and LUMO) delocalization in  $P^0$ ,  $P^+$ , and  $P^-$  molecules, as calculated with DFT B3LYP/6-31G(d)

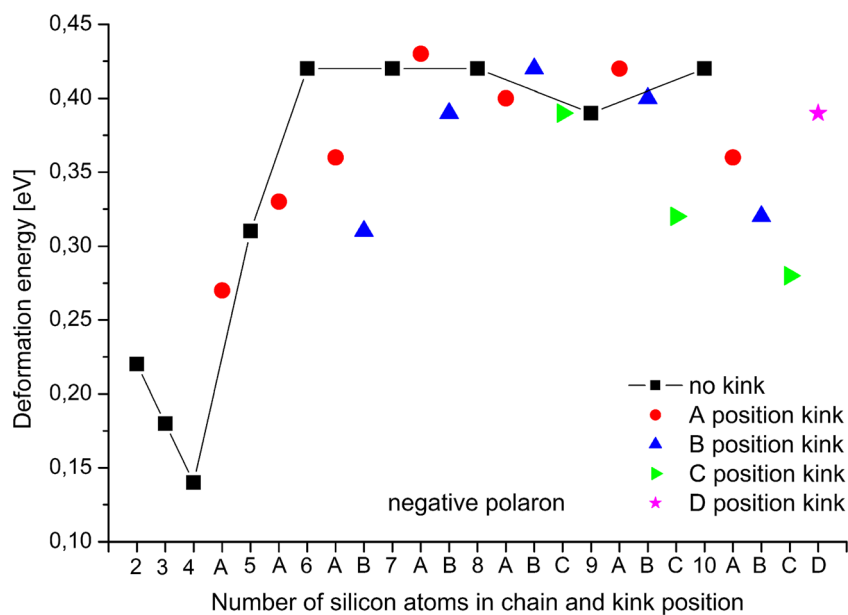
**Fig. 9**  $E_{\text{def}}$  of each OMPSi<sub>n</sub> in the form of a positive polaron

parts of kinked chains. Even in the symmetrical case (**10D**), the HOMO is located only on one part of the backbone. The LUMOs of P<sup>-</sup> are also strictly localized on the phenyl ring, as in P<sup>+</sup> molecules, but they are located at different positions. They are distributed on the phenyls attached to Si numbers 9 and 10, and they ignore the presence of the kink and its position.

#### Polaron binding energy and deformation energy

The polaron binding energy ( $E_p$ ) consists of two terms: the deformation energy ( $E_{\text{def}}$ ) and the electron-photon energy

( $E_{\text{el-ph}}$ ). Since segments can move relatively easily in oligomer molecules,  $E_{\text{def}}$  comprises most of  $E_p$  (about 90 %) for such molecules. Therefore,  $E_{\text{def}}$  was plotted for the positive and negative polaron quasiparticles derived from all of the studied oligomers, and these are displayed in Figs. 9 and 10, respectively. First, let us consider OMPSi<sub>n</sub> without the kink defect. As can be seen, both graphs can be divided into parts associated with very short oligomers (2–4 units) and with longer chains. For P<sup>+</sup>,  $E_{\text{def}}$  decreases rapidly with oligomer length until the pentamer, after which the decrease in  $E_{\text{def}}$  is much more gradual. Our investigation of geometries revealed that there is a significant influence of the relaxation process on

**Fig. 10**  $E_{\text{def}}$  of each OMPSi<sub>n</sub> in the form of a negative polaron

**Table 1** Values of  $E_{\text{def}}$ ,  $E_{\text{el-ph}}$ , and  $E_{\text{p}}$  in eV, as calculated according to [10] (estimated values are shown in italics)

Molecule	$P^+$			$P^-$		
	$E_{\text{p}}$	$E_{\text{def}}$	$E_{\text{el-ph}}$	$E_{\text{p}}$	$E_{\text{def}}$	$E_{\text{el-ph}}$
<b>2</b>	0.43	0.42	0.01	0.37	0.22	0.15
<b>3</b>	0.26	0.25	0.01	0.31	0.18	–
<b>4</b>	0.23	0.23	–0.01	0.27	0.14	–
<b>4A</b>	0.44	0.43	0.01	0.40	0.27	–
<b>5</b>	0.21	0.23	–0.02	0.45	0.31	0.14
<b>5A</b>	0.27	0.27	0.00	0.48	0.33	0.15
<b>6</b>	0.17	0.20	–0.03	0.54	0.42	0.12
<b>6A</b>	0.25	0.27	–0.02	0.47	0.36	0.11
<b>6B</b>	0.18	0.20	–0.02	0.42	0.31	0.11
<b>7</b>	<i>0.19</i>	0.19	–	0.55	0.42	0.13
<b>7A</b>	<i>0.17</i>	0.18	–	<i>0.55</i>	0.43	–
<b>7B</b>	<i>0.19</i>	0.16	–	<i>0.56</i>	0.39	–
<b>8</b>	<i>0.27</i>	0.18	–	<i>0.52</i>	0.42	–
<b>8A</b>	<i>0.18</i>	0.26	–	<i>0.55</i>	0.39	–
<b>8B</b>	<i>0.17</i>	0.17	–	<i>0.53</i>	0.42	–
<b>8C</b>	<i>0.16</i>	0.16	–	<i>0.55</i>	0.39	–
<b>9</b>	<i>0.25</i>	0.15	–	<i>0.52</i>	0.39	–
<b>9A</b>	<i>0.25</i>	0.24	–	<i>0.52</i>	0.42	–
<b>9B</b>	<i>0.15</i>	0.24	–	<i>0.55</i>	0.40	–
<b>9C</b>	<i>0.15</i>	0.14	–	<i>0.53</i>	0.32	–
<b>10</b>	<i>0.23</i>	0.14	–	<i>0.45</i>	0.42	–
<b>10A</b>	<i>0.16</i>	0.22	–	<i>0.55</i>	0.36	–
<b>10B</b>	<i>0.14</i>	0.15	–	<i>0.49</i>	0.32	–
<b>10C</b>	<i>0.14</i>	0.13	–	<i>0.45</i>	0.28	–
<b>10D</b>	<i>0.19</i>	0.13	–	<i>0.41</i>	0.39	–

the geometries of short oligomers. Hence, the higher values of  $E_{\text{def}}$  can be explained by this considerable change in geometry (e.g., bond lengths).

Negative polarons show a different trend in  $E_{\text{def}}$  with oligomer length. Surprisingly (considering the conclusion of the previous paragraph), in this case the longer oligomers show higher deformation energies. However, the bond angles must be also taken into account when describing the geometry, and it is worth noting that (as depicted in Fig. 4) the highest difference between the neutral molecule and the  $P^+$  decamer is  $6^\circ$ , whereas the highest difference between the  $P^0$  and  $P^-$  OMPSi<sub>10</sub> is  $15^\circ$  (bond number 6).

Hence,  $P^-$  relaxation greatly affected some bond angles, and these particular changes in geometry were probably more influential than the changes in bond lengths, leading to an increased  $E_{\text{def}}$  for the longer oligomers.

Table 1 summarizes all of the computed  $E_{\text{p}}$ ,  $E_{\text{def}}$ , and  $E_{\text{el-ph}}$  values. It is clear that the difference between  $E_{\text{p}}$  and  $E_{\text{def}}$  is given by  $E_{\text{el-ph}}$ , which seems to have a similar value for all oligomers (although many of the  $E_{\text{el-ph}}$  values for the longer oligomers were not computed due to the excessive computational time required to do so). The average value for positive

polarons is  $|0.01|$  eV and that for negative polarons is  $|0.13|$  eV. Note that  $E_{\text{def}}$  for  $P^-$  quasiparticles is no smaller than  $E_{\text{def}}$  for  $P^+$  quasiparticles, but  $E_{\text{p}}$  for  $P^-$  quasiparticles is significantly higher than  $E_{\text{p}}$  for  $P^+$  quasiparticles, which means that the  $E_{\text{el-ph}}$  contribution for  $P^-$  quasiparticles is much higher than the corresponding contribution for  $P^+$  quasiparticles. To summarize the whole situation for  $E_{\text{p}}$ , Table 1 also displays estimated  $E_{\text{p}}$  values (in italics) for the molecules for which  $E_{\text{el-ph}}$  could not have been computed. They were estimated by adding 0.01 eV to  $E_{\text{def}}$  or  $P^+$  and adding 0.13 eV to  $E_{\text{def}}$  for  $P^-$ , respectively.

## Conclusions

A computational investigation of oligo[methyl(phenyl)silylene]s into which a kink was introduced, leading to the disruption of the backbone conformation, revealed that this defect exerts a significant influence on the relaxation processes of positive and negative polaron quasiparticles. In particular, the spin density distribution is sensitive to the presence of the conformational anomaly.



Overlaps between molecular orbitals and the delocalization of these orbitals are disturbed, which has a direct impact on the electron distribution. When the kink is inserted such that it divides the chain into longer and shorter parts, the delocalized HOMOs are shifted towards the longer part. The LUMOs are only delocalized on the phenyl rings in the  $P^+$  and  $P^-$  quasiparticles, and this delocalization is seemingly independent of the presence of a kink. In the  $P^+$  quasiparticles, the LUMOs are located on the central phenyls, whereas they are on the edge phenyls in the  $P^-$  quasiparticles.

While the spin distribution is significantly affected, the charge distribution is only slightly influenced by the introduction of a kink. There are differences between  $P^0$ ,  $P^+$ , and  $P^-$  in the central region of the backbone. However, the introduction of the kink does not cause a substantial charge redistribution.

The change in the deformation energy, which is the change in energy associated with the process of relaxation from the neutral molecule to the polaron quasiparticle, was found to present opposite trends for  $P^+$  and  $P^-$ . This is because the change in deformation energy is related to changes that occur to the geometry of the oligosilylene. Nevertheless, the shorter chains can easily adjust their geometries during the relaxation process, whereas longer chains can undergo larger changes in geometry but those changes only occur to a particular part of the chain.

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