



Conformational disorder in polysilylenes studied theoretically on tetramers



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ABSTRACT

DFT calculations with B3LYP, M06 and ω B97X-D functionals with 6-31G* basis set are used for a study of non-bonding intramolecular interactions in tetra[methyl(phenyl)silylene] (MPSi₄), tetra[(dimethyl)silylene], tetra(silylene) (Si₄) and further in molecules of tetra[cyclohexyl(methyl)silylene] and carbon chain analogue of MPSi₄. A tetramer can serve as a model for conformational defect – a kink that is worth to understand especially in case of polysilylenes. The kink disruptions are viable in poly[methyl(phenyl)silylene], poly[(dimethyl)silylene] as well as in poly[cyclohexyl(methyl)silylene] chains because the energy profiles of their oligomer analogues go through minimum in *gauche* conformation and moreover they are significantly stabilized by non-bonding interactions (either π - π or Van der Waals). The molecule of Si₄ is more flexible and keeping of a kinked conformation is less probable due to lower energy barriers in its energy profile. The functional ω B97X-D was found to be reliable in approaching real conformer distribution. TDDFT analysis of conformation impact on frontier molecular orbital density distribution and electronic transitions was performed for MPSi₄ to contribute understanding of the influence of conformational disorder on electronic properties of one of the most practically important member of polysilylene group of polymers.

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1. Introduction

Among polymers, linear polysilanes called polysilylenes (and other linear polymers with backbone made from heavier atoms of the fourth main group from periodical table of elements) have special position due to σ -conjugation along their main chain which does not require alternating scheme of single and double bonds as in π -conjugated carbonaceous polymers. Some of the polysilylenes have aromatic substituents in positions of polymer side groups which imparts even more complicated electronic properties due to mixing of σ - and π -delocalized systems [1]. A great effort has been developed to synthesize, characterize and explain all observed phenomena including theoretical works [2,3]. Exhaustive studies on oligomeric model molecules in order to approach long chain polymer properties by extrapolation have been performed too [4,5]. The topic seemed to be covered, and relatively quiet for a long time with a stable interpretational framework. However, the last findings in the field of thin films, which are made from these polymers [6,7], or conductive π -conjugated systems [8,9] and even general polymers [10–13], revived interest on the impor-

tance of polymer chain ordering, stacking, H or J aggregate formation, chain alignment, and dependence of the material properties on the development of the film thickness starting from sub-molecular cover degree through thin films from several to hundreds nanometres up to micrometric thickness. Among other factors, conformational disorder play crucial role in development of various structural features and properties emerging with increasing thickness of polymer films.

As has been cited above, poly and oligosilylene conformational studies have been successfully performed in the past [14,15], however, with respect to the need of proper interpretation of conformational defects in the polysilylene material structure, more recently developed calculation methods are expected to be especially useful in identification of contribution of long range interactions. Polysilylene chains are not purely rod-like in shape. It has been already shown, that they are able to adopt geometry with bends between conjugated linear segments. The smallest conformational unit of a bend structure can be regarded as four consecutive silicon (Si) atoms arranged in approximately *gauche* conformation and is also called a kink [16,17]. Such kinks are interruptions of a regular backbone arrangement (helical, zig-zag) and they can be considered as local conformational defects that disrupt σ -electron delocalization resulting in the changes in electronic properties of material [18–21]. Although a whole family of various

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defects can occur in polysilylene solid phase, the kink is the simplest one but omnipresent, hence, extremely important and worth of attention.

It has been already shown experimentally as well as theoretically [22] on model oligo[methyl(phenyl)silylene] molecules and thus poly[methyl(phenyl)silylene] (PMPSi) that Si backbone conformation and presence of a kink defect and its position influence energy levels and spatial distribution of molecular orbitals. Further, a kink also affects spin density distribution in charged (cations and anions) analogues modelling polarons in real solid state polymers [23,24]. In spite the dramatic effect of the kink on the structure of electronic levels, the total energy of neutral molecule is not significantly increased by virtual introduction of a kink as has been demonstrated in our previous work [25].

In order to clarify specific structure-property relationships we present a conformational study in this field. The kink is considered as four consecutive Si atoms ideally in *syn* conformation, whose dihedral angle (ω) corresponds to 0° . Tetrasilylenes are the smallest and most tractable model molecular units that can be used for construction of the kinked molecule as well as other backbone conformations. Several studies of linear tetrasilylenes with small substituents, such as hydrogen, methyl or halogen, were described in Refs. [26,27]. These tetrasilylenes were found in the almost whole range of ω as enantiomeric pairs with one exception of conformation 180° (*anti*) and with local minima representing angles $\omega = \pm 40^\circ$ (*cisoid*), $\omega = \pm 60^\circ$ (*gauche*), $\omega = \pm 90^\circ$ (*ortho*), $\omega = \pm 150^\circ$ (*deviant*) and $\omega = \pm 165^\circ$ (*transoid*). Conformation *syn* is thus unfavourable even for polysilylenes with small side groups [27]. Therefore, hydrogen, methyl, cyclohexyl and phenyl groups were chosen as side groups to build a suitable set of models including tetra(silylene) (Si_4), tetra(dimethyl)silylene (DMSi₄), tetra(cyclohexyl(methyl)silylene) (cyc-HMSi₄) and tetra[methyl(phenyl)silylene] (MPSi₄). The choice of model side groups is also practically relevant as poly[(dimethyl)silylene], poly[cyclohexyl(methyl)silylene] and namely PMPSi are the most reported polysilylene materials in experimental literature [28]. Moreover, absorption spectra and molecular orbitals are investigated for MPSi₄ to complete our research in the topic of kink as conformational defect in polysilylenes. It is expected that the adoption of kinked arrangement is significantly influenced by different steric limitations of chosen groups, attractive or repulsive interactions of phenyl groups or other non-bonding interactions of side groups. It is important to note that these groups also affect the main chain, namely aromatic substituents. Beside, a molecule with carbon atoms inserted instead of Si was also studied although the calculations were limited only to 1,2,3,4,5,6-hexamethyl-2,3,4,5-tetraphenylhexane (MPC₄) with methyl and phenyl groups in the same arrangement as MPSi₄ and considering the other purely carbonaceous analogues are known and trivial. A five membered (Si_4 , DMSi₄, cyc-HMSi₄, MPSi₄ and MPC₄) set of models was defined in this way.

The aim of this paper is to investigate the above introduced set of models with DFT computational analysis of molecular arrangement and energy. In addition, electronic properties of MPSi₄ are described by time dependent DFT (TDDFT) in second part of this study because they can reveal a relation between absorption maximum and the employment of π - π interactions corresponding to various backbone conformations. Density functionals were chosen with the respect of involvement of the dispersion term [29,30]. The B3LYP functional is considered as a good tool for various types of calculations although it suffers on underestimation of long range (non-bonding) interactions. This can be improved by the utilization of M06 functional which has 27% of HF exchange and has a very good response under dispersion forces [31]. On the other hand, the non-Coulomb part of exchange functionals typically dies off too rapidly and becomes very inaccurate at large distances. Therefore, empirical dispersion can be implemented to deal successfully

such calculations, e.g. the ω B97X-D [32]. The above described selection of functionals allows a virtual experiment based on comparison of three calculated conformational energy profiles with different extent of long range interactions involvement. Hence, it is expected that the rising contribution of non-bonding interactions will be manifested as increasing either positive, or negative energy difference for each conformer calculation enabling thus conformational analysis and comparison between tested model molecules with different chemical structure.

2. Computational methods

All calculations were performed with Spartan 14 software [33]. Studied MPSi₄, DMSi₄, Si₄, cyc-HMSi₄ and MPC₄ were modelled in several conformations. Dihedral angle ω was constrained by a step of 10° to following values $0^\circ, 10^\circ, \dots, 180^\circ$ and further from -170° to -0° (which means that 360° corresponds to -0°) for MPSi₄, while ω of DMSi₄ and Si₄ was constrained to values $0^\circ, 10^\circ, \dots, 180^\circ$. The investigated range of angle was also 0 – 180° for cyc-HMSi₄ and MPC₄, however the increment of the angle value was set to 20° because these molecules served as reference models in the study for comparison of phenyl vs. cyclohexyl group and Si conjugated vs. carbon non-conjugated backbone influences. The edge atoms of all types of molecules with exception of Si₄ were capped with methyl groups. Further, molecules were treated as isolated in a vacuum environment. In total, 37 structures of MPSi₄, 19 structures of DMSi₄ and Si₄ and 9 structures of cyc-HMSi₄ and MPC₄ were subjected, first, to geometry optimization by B3LYP/6-31G* and then to single point energy calculation with M06 and ω B97X-D functionals involving dispersion terms to describe energy contribution of weak interactions in the dependence on ω . In addition, another approach MP2/6-311++G** was applied to energy calculation of simplest cases of oligosilylenes (Si₄ and DMSi₄) to check if this theory has significant impact to obtained results for studied molecules and to compare it with DFT functionals.

Excitation properties were calculated for ten chosen conformers of MPSi₄ with $\omega = 0^\circ, 20^\circ, \dots, 170^\circ$. TDDFT was used with B3LYP, M06 and ω B97X-D functional and 6-31G* basis set for single point energy calculation of absorption wavelengths, intensities and other excitation properties. Obtained spectra were compared to evaluate suitability of the used functionals for TDDFT calculation of silylene molecules.

2.1. Chemical formulas of used model molecules

In order to make understanding of the reader to the text easier, formulas of all investigated molecules are shown in Fig. 1 together with their various names that can be found throughout the cited literature.

3. Results and discussion

3.1. Conformational analysis

Virtually prepared tetrasilylenes and their various analogues were subjected to geometry optimization in several conformations of Si backbone corresponding to various constrained values of ω . Designation of molecules is through the whole paper consistent and is composed from the type of tetramer and the value of ω , for example MPSi_{4_120}.

Fig. 2 shows energy profile of MPSi₄ corresponding to conformational energy dependence of MPSi₄ in the ω range from 0° to 360° , i.e. from 0° to -0° . Conformation with $\omega = 0^\circ$ has the highest energy, therefore, it has been set as the reference level for all

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