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Ab Initio Studies on Silicon Compounds. 3.† The Trans–Gauche Mixed Structure of Parent Polysilane

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Abstract: Ab initio crystal orbital calculations are performed on the electronic structures of parent polysilanes having a unit cell periodicity consisting of n trans links and one gauche link (GT_n) and having their combined structures ($GTGT_m$). Koopmans' ionization potential, vertical electron affinity, and effective mass of electron and hole are systematically estimated for $n = 1, 3, 5, 7, 9$, and $m = 3, 5$. The results show that the gauche links only slightly disturb σ-conjugation. Both electrons and holes are not confined to the trans segments but are highly delocalized along an entire chain.

1. Introduction

Polysilane is a σ-conjugated polymer with a silicon–silicon backbone whose energy band structure corresponds to that of a one-dimensional semiconductor.[1] Semiconducting properties such as photoconduction, photoluminescence, and nonlinear optical effect have been observed in many kinds of organopolysilanes with alkyl or aryl substituents.[2] The band structures of parent polysilanes with homogeneous helical chain conformations were studied in our last paper.[3] The results showed that a trans conformer is the ground state of polysilane and that *trans*-polysilane has a smaller band gap, lower ionization potential, and greater electron delocalization than *gauche*-polysilane.

Recent measurements of the temperature dependence of carrier mobility suggest that photocurrent conducts via a hopping transport of localized holes.[4] It has been reported that the hole localization occurs due to the existence of various inhomogeneous chain structures, especially gauche links.[5] Kligensmith et al.[6] calculated the highest occupied molecular orbital (HOMO)) and the lowest unoccupied molecular orbital (LUMO) of $Si_{20}H_{42}$ oligomers containing a gauche link by the semiempirical INDO/S method. They reported that the HOMO localizes within the longest trans segment and the LUMO remains largely delocalized.

In this article, the energy band structures of the parent polysilane, having a unit cell consisting of n trans links and one gauche link (denoted by T_nG) and having their combined structures (denoted by $GTGT_m$), are calculated by the ab initio crystal orbital method. Koopmans' ionization potential (IP), vertical electron affinity (EA), and effective mass of electron and hole are systematically estimated for $n = 1, 3, 5, 7, 9, m = 3, 5$ and all-gauche (GG) and all-trans (TT) structures.

2. Method of Calculation

The ab initio crystal orbital method was used with a combined symmetry operation[7] rather than with a simple translation to obtain the electronic structure of the polysilane. Each T_nG structure, with odd numbers of n, has a screw axis coincident with the Cartesian z axis and a helical angle of 120°, where the unit cell consists of $(n + 1)$ silicon atoms and $2(n + 1)$ hydrogen atoms. The polymer structures of TG and T_3G polysilanes are schematically shown in Figure 1. The perspective end views of the T_nG polysilanes (n is an odd number) are regular triangles. The T_nG polysilanes for even numbers of n, on the other hand, have a variety of complex polymer structures. The calculation in this paper has been restricted to only the odd-number cases ($n = 1, 3, 5, 7$, and 9). Each $GTGT_m$ structure, with odd numbers of m, also has a screw axis coincident with the z axis and a helical angle of 120°, where the unit cell consists of $(m + 3)$ silicon atoms and $2(m + 3)$ hydrogen atoms.

We have used the STO-3G basis set.[8] The geometrical parameters used here are previously reported values optimized for a trans conformer.[9] The helical angle for a gauche conformer was set to 90°, corresponding to the dihedral angle of 60°.[10] For other conformers, the rigid rotor approximation is employed throughout this study. The number of neighboring unit cells is determined as the interaction radius approaches 120 au, i.e., 22, 19, 16, 9, 6, 4, 3 for GG, TG, TT, T_3G, T_5G, T_7G, T_9G,

Table I. Total Energy of All-Trans (TT), All-Gauche (GG), and Trans–Gauche Mixed Structures of Parent Polysilanes

	energy, au	
structures	per unit cell	per SiH_2
GG	−573.583 628	−286.791 814
TG	−573.584 220	−286.792 110
T_3G	−1 147.169 131	−286.792 283
T_5G	−1 720.754 048	−286.792 341
T_7G	−2 294.338 982	−286.792 372
T_9G	−2 867.923 928	−286.792 393
TT	−573.584 924	−286.792 462
$GTGT_3$	−1 720.753 348	−286.792 225
$GTGT_5$	−2 294.338 287	−286.792 286

and 6, 4 for $GTGT_3$, $GTGT_5$, respectively. The cell-wise summation scheme is used for the cutoff of the integrals.[11] Density matrices are obtained by using Simpson's rule with the regular interval sampling of 81k points, about half of the Brillouin zone.[12]

We recently found that computational results, especially the total energy, are sensitive to the truncation threshold of the two-electron integrals when the large interaction is included in the calculation.[13] For example, preliminary test calculation for the TT conformer showed that the total energies were −573.584 723, −573.584 923, and −573.584 918 au, corresponding to the threshold values of 10^{-6}, 10^{-8}, and 10^{-10}, respectively. A threshold value of 10^{-8} was used throughout the present study.[14]

The effective mass of the hole at the valence band edge and that of the electron at the conduction band edge are calculated by

$$m^* = \hbar^2/(d^2\epsilon(k)/dk^2) \tag{1}$$

where $d^2\epsilon(k)/dk^2$ is numerically determined by the least-squares fits of the calculated band structures.[15] The effective mass is an important

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(9) The optimized structure of *trans*-polysilane is as follows (from ref 3): $r_{Si-Si} = 2.245$ Å, ∠Si-Si-Si = 114.1°, $r_{Si-H} = 1.425$ Å, ∠H-Si-H = 106.0° (STO-3G basis set), $r_{Si-Si} = 2.382$ Å, ∠Si-Si-Si = 112.4°, $r_{Si-H} = 1.485$ Å, ∠H-Si-H = 107.8° (DZ basis set). The qualitative results on helical angle dependences of total energy, IP, EA, and effective mass are almost the same for these basis sets. Therefore, in this work, we have used the STO-3G basis set.

(10) The relation between the helical angle θ and the dihedral angle τ is given as: $\cos \theta = 1/2(-\cos \phi + \cos \tau - \cos \phi \cos \tau - 1)$, where ϕ is the bond angle (Shimanouchi, T.; Mizushima, S. *J. Chem. Phys.* **1955**, *23*, 707).
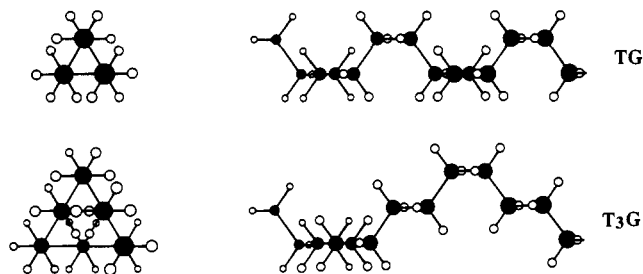
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(14) Our previous work employed threshold values of 10^{-6}.

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Figure 1. Schematic views of TG and T₃G polysilanes. The left figures are perspective end views and the right are side views. The large circle indicates a silicon atom and the small circle a hydrogen atom.

Table II. Koopmans' Ionization Potential (IP), Vertical Electron Affinity (EA), and Effectiive Masses of Electron (m_e^*) and Hole (m_h^*) for Parent Polysilanes with Various Structures[a]

structure	IP, au	EA, au	m_h^*	m_e^*
GG	0.299	0.385	10.25	1.04
TG	0.269	0.355	0.56	0.76
	(0.270)	(0.341)		
T₃G	0.257	0.329	0.41	0.39
	(0.255)	(0.319)		
T₅G	0.252	0.318	0.34	0.31
	(0.250)	(0.312)		
T₇G	0.249	0.312	0.32	0.28
	(0.247)	(0.308)		
T₉G	0.247	0.308	0.30	0.27
	(0.246)	(0.306)		
TT	0.240	0.297	0.15	0.10
GTGT₃	0.261	0.336	0.47	0.56
	(0.260)	(0.326)		
GTGT₅	0.256	0.324	0.42	0.53
	(0.255)	(0.319)		

[a] The values in parentheses are the weighted average values of GG and TT polysilanes. Units of effective mass are in mass of a free electron.

index for the semiconductive materials because an electron carrier conducts as a particle with mass m^* in the external electric field.

3. Results and Discussion

According to results[3] for the helical angle dependence of total energy in parent polysilanes, there are two energy minima at 87.5° (gauche) and 180° (trans)[10] and the *trans*-polysilane is more stable than the *gauche*-polysilane by 0.38 kcal/mol per SiH₂ unit at the STO-3G and tenth neighbors level. Table I lists the total energy of parent polysilanes with TT, GG, T$_n$G, and GTGT$_m$ structures (n = 1, 3, 5, 7, 9, and m = 3, 5). Total energy decreases with increases in the length of the trans segment, which is consistent with the result that *trans*-polysilane is more stable than *gauche*-polysilane.

The energy band structures of parent polysilanes with TG and T₃G structures are shown in Figure 2. The results for the other structures are not shown because of their complexity, but their main characteristic values, that is, IP, EA and effective masses of electron and hole, are listed in Table II along with the values for other structures. Three essential effects of a gauche link along a trans chain can be understood from Figure 2 and Table II: effective mass, IP and EA, and band splitting.

The effective mass of the hole (m_h^*) at the valence band edge and that of the electron (m_e^*) at the conduction band edge are calculated from eq 1. A large (small) curvature is due to strong (weak) σ-conjugation along a chain and corresponds to small (large) effective mass and spatial delocalization (localization). The results in Table II show that both m_h^* and m_e^* are smaller than unity, except in the case of the GG structure. They both decrease with increases in n. When n = 9, m_h^* and m_e^* are 0.30 and 0.27, respectively. Furthermore, m_h^* and m_e^* in GTGT$_m$

Table III. Band Widths of the Highest Valence Band (VB) and the Lowest Conduction Band (CB) in GG, TT, and GT$_n$ Structures

structures	VB width, au	CB width, au
GG	0.0290	0.0215
TG	0.0555	0.0642
T₃G	0.0428	0.0437
T₅G	0.0270	0.0271
T₇G	0.0175	0.0175
T₉G	0.0118	0.0118
TT	0.1401	0.2073

structures are also smaller than unity and their values are almost equal to the averaged values between those of GT and GT$_m$ structures. This means that the electrons and holes are not localized in the longer trans segments but are delocalized along a chain, even if gauche links exist in the *trans*-polysilane.

IP and EA decrease with increasing n, which indicates a systematic narrowing of the energy band gap between the conduction and the valence bands.[16] It is well-known experimentally that increasing the polymerization degree in the oligosilane results in decreasing IP[17] and Eg.[2] It has been concluded in the above discussion, however, that both electrons and holes in T$_n$G polysilanes are not confined to the trans segment and delocalize along an entire chain. The n dependence of IP (EA) and the energy gap, therefore, does not originate from variations in conjugation length. The IP and EA values, in parentheses in Table II, are calculated by the following equations.

$$IP(T_nG) = (nIP(TT) + IP(GG))/(n + 1) \qquad (2)$$

$$IP(GTGT_m) = ((m + 1)IP(TT) + 2IP(GG))/(m + 3) \qquad (3)$$

The equations for EA are similar to these equations. Equations 2 and 3 estimate the weighted average values of IP(EA) in *all-trans*-polysilane and *all-gauche*-polysilane. These average values coincide with values calculated by the ab initio method. This also indicates that electrons and holes are delocalized well along a chain. The IP of T$_n$G converges to that of TT with an asymptotic form of $1/n$. When n is the polymerization degree, on the other hand, the value of IP converges to the value of infinite polysilane with an asymptotic form of $1/n^2$.[18] The rod-to-coil transition model[19] for thermochromism assumes perfect cutting of conjugation by a gauche link. This model, therefore, overestimates the n dependence of the optical properties.

The previous discussions were restricted to the n dependence of the band structures in T$_n$G polysilanes in the vicinity of the band edges. Next, variations in the band structures will be discussed in the part lower than IP and the part higher than EA. These structures can be systematically understood by the following idea of zone folding. When the unit cell length of a polymer is d, the k value of the Brillouin zone edge is π/d. If the unit cell length is set at twice ($2d$), the resulting band structure is the same as a structure formed by folding back band profiles obtained for a unit cell of length d at the half point of the k axis ($\pi/2d$).[20] The unit cell length of the T₃G polysilanes is just double that of the TG polysilanes. Figure 2 shows that the band structure of T₃G can be approximately obtained by folding back the TG polysilane band structure at the half k point. This zone folding effect results in band splitting or multi-folding. Similarly, the band structures of T₅G, T₇G and T₉G are obtained by folding the TG band structure three, four and five times, respectively. The band width of the highest valence band and the lowest conduction band de-

(15) See, for example: Kittel, C. *Introduction to Solid State Physics*; 5th ed.; Wiley: New York, 1976; pp 218–219.

(16) Energy gap values obtained by use of the ab initio method do not coincide well with experimental values. This work should be limited to the qualitative discussions. Excitonic effects should be considered for the further calculations.

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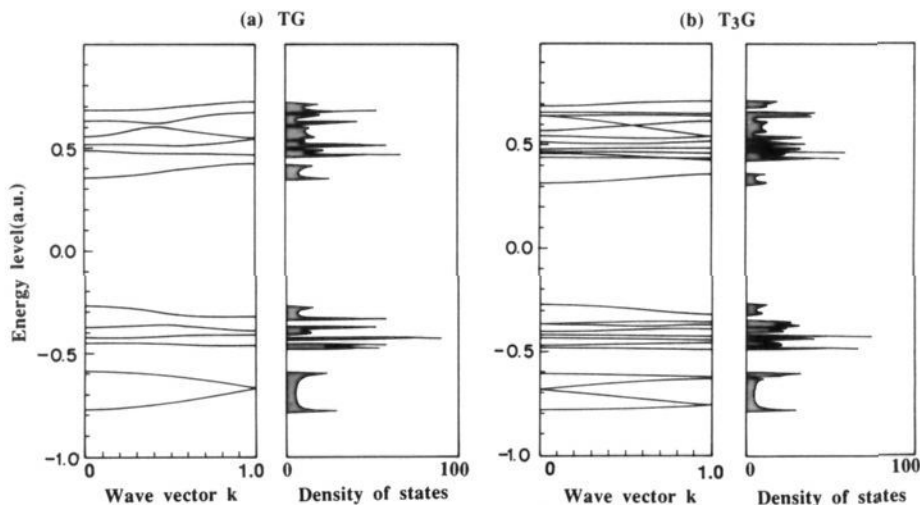
Figure 2. Calculated band structures of (a) TG and (b) T_3G polysilanes.

G T T T G T G T T T G T G T T T G T G

Figure 3. Size (bar length) and sign (bar color) of the coefficients of the backbone Si sp^3 orbitals in the HOMO of $GTGT_3$ polysilane. The silicon atoms are symbolized by circles.

creases with successive folding procedures, as listed in Table III. Since their Brillouin zone width decreases at the same time, this band narrowing effect is consistent with decreases in the effective mass.

Kligensmith et al.[6] reported that the HOMO localizes withiin the longest trans segment in the $Si_{20}H_{42}$ oligomer of a trans conformation with a gauche link in the backbone (segment model). However, it has been clearly shown by our ab initio calculations that both electrons and holes are highly delocalized in the trans–gauche mixed structures. This delocalization can be visualized by the AO coefficients distribution of the HOMO along a chain with $GTGT_3$ structure as shown in Figure 3.[21] The spatial profile shows that the HOMO does not localize mainly in the longer T_3 segments but delocalizes well along a chain. We think that this significant difference with the segment model originates from the calculation method difference (INDO/S and HF/

(21) Although we have used only valence orbitals (3s and 3p) for this transformation, the HOMO calculated by use of the ab initio method cannot be described exactly by the Si–Si hybrid sp^3 valence orbitals, unlike the semiempirical method where the basis set consists of only valence orbitals. Figure 3 should be considered to be an approximate picture.

STO-3G) rather than from the chain length difference (Si_{20} and $Si_∞$). It may be a successive important study to compare the results calculated by the different methods for the same $Si_{20}H_{42}$ oligomer. Furthermore, there are important differences between periodic gauche links and random ones. The intent here is to show the gauche links do not produce the sharp localization of the segment model. The effect of random distribution of gauche links on the delocalization is an important problem to be studied. It is also important to study the effect of longer gauche chains or the existence of plural phases with multiconformations in real organopolysilane samples.[22]

4. Conclusions

Our studies of the electronic structures of parent polysilanes with trans–gauche mixed structures employing the ab initio Hartree–Fock crystal orbital method at the STO-3G level gave the following results.

The effective mass of electron and hole is smaller than unity and decreases further below 0.3 with increases in trans segment length. This means that electrons and holes are not strongly localized in the trans segment, but delocalized along a chain in trans–gauche mixed structure polysilanes.

Ionization potential and electron affinity decrease with increasing trans segment length. Their values coincide with the weighted average values for *all-trans-* and *all-gauche*-polysilanes.

The band structure of T_nG polysilane can be approximately obtained by folding back the band profile of TG polysilane. This zone folding effect results in narrowing of the band widths in the highest valence and lowest conduction bands.

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