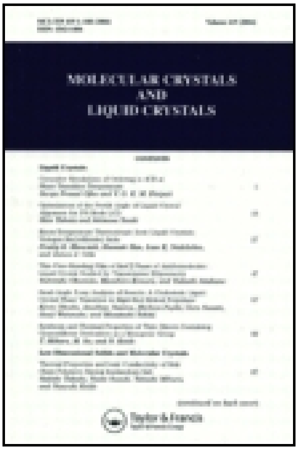

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The Electronic Structures of Permethyl Oligogermane Radical Cation with Longer Chains

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The Electronic Structures of Permethyl Oligogermane Radical Cation with Longer Chains

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Hybrid density functional theory (DFT) calculations have been carried out for neutral and radical cation of permethyl-oligogermane, $Ge_n(CH_3)_{2n+2}$ ($n = 4$–28), to elucidate the electronic structures at ground and low-lying excited states. It was found that a hole is distributed in both the Ge-Ge skeleton (main chain) and methyl group (side chain) in the case of shorter chain-lengths below $n = 8$, whereas the spin density (hole) in the methyl group becomes significantly smaller in longer chain-lengths ($n > 10$). The IR-band of radical cation were assigned on the basis of theoretical calculations.

Keywords: oligogermane; hole transfer; radical cation; DFT; PBC

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INTRODUCTION

Polysilanes and polygermanes have been extensively investigated because of their potential utility as electron and hole transport materials in organic multilayer light emitting diodes (LEDs), one-dimensional semi-conductors, photo-resist materials, and high-density optical data storage materials [1–10]. The values of mobility in the order of 10^{-4} to $10^{-3}\,cm^2V^{-1}s^{-1}$ were observed for the oligogermanes, which correlates strongly with the electron and hole conductivities as an organic semi-conductor. Hence, determination of the electronic structures of ionic states at both ground and excited states is an important theme in development of new materials of germane systems.

The experimental works have been carried out by several groups. The electronic absorption spectroscopy is convenient technique to determine the electronic excited states of polygermanes. Mochida *et al.* [11,12] measured the transient- and steady state-absorption spectra of radical ions of oligo- and polygermanes with aryl-group. The spectra have two peaks in UV and near-IR regions as well as those of polysilanes, and the maxima in both spectra are shifted to longer wavelengths with increasing chain length.

The ionization potential [13,14] of several kinds of oligo- and polygermanes were reported, for example, $n = 4$ and 10 permethyl oligogermanes are 7.80 and 5.55 eV, respectively. And the values of polygermanes are reported in the 5.31–5.68 eV region and roughly depend upon side chain length and degree of polymerization.

In previous works, we investigated the structures and electronic states of the polysilane radical cation by means of semiempirical PM3-CI [15] and density functional theory (DFT) [16] method. The permethyl oligosilane $Si_n(CH_3)_{2n+2}$ was chosen as a model of polysilane. We showed that excess electron and hole are fully delocalized along the skeleton of linear polysilane. The electronic excitation energy from the ground to first exited states was gradually red-shifted as a function of the number of chain Si atoms (n). Our previous studies suggested that the excess electron and hole are not localized in the case of the regular all-trans form in the linear polysilane but is delocalized widely along the main chain. Also, mechanism of electron localization at finite temperature was investigated by means of MM2 molecular dynamics and PM3 methods [17].

In the present study, DFT calculations have been carried out for neutral and radical cation of the linear permethyl oligogermane with long-chain $Ge_n(CH_3)_{2n+2}$ ($n = 4$–28) in order to determine the electronic structures.

COMPUTATIONAL METHOD

Almost all of the present calculations were carried out at the DFT(B3LYP)/3-21G(d) level of theory. A linear oligogermane with methyl groups in side-chain, permethyl oligogermane ($Ge_n(CH_3)_{2n+2}$) ($n = 4$–28), was examined. First, the initial geometries of neutral oligogermanes were made by MM2 calculation. Using the optimized geometry of the MM2 calculation, the geometries of neutral and cationic oligogermanes were optimized at the B3LYP/3-21G(d) level of theory. The excitation energies were calculated by means of time-dependent (TD) DFT calculations. Six excited states were solved in TD-DFT calculations. All hybrid DFT calculations were carried out using Gaussian03 program package [18]. Note that this level of theory gives reasonable features for several molecular device systems [16,19–22].

RESULTS AND DISCUSSION

A. Band Structure of Poly(Dimetylgermane)

To elucidate the electronic structures of neutral polygermane in details, a band structure is calculated at the B3LYP/3-21G(d) level of theory. The model of the infinite length poly(dimethylgermane) is calculated as using one-dimensional periodic boundary condition (PBC). The unit cell used in this calculation shows in Figure 1. The optimized geometrical parameters are given in Table 1. The Ge-Ge bond lengths are calculated to be 2.4148 and 2.4184 Å, 2.4125 Å, respectively. The result is plotted in Figure 1. At the center of the Brillouin zone ($k = 0$), the band gap is calculated to be 4.27 eV. On the other hand, the band gap becomes wider at the edge of the Brillouin zone ($k = \pi/a$). This result indicates that the doping is necessary to produce the carrier in the poly(dimethylgermane). Also, the band gap calculated by periodic condition is in good agreement with that of oligogermane ($n = 28$: 4.28 eV). This suggests that the longer oligogermanes exhibits the electronic properties of polygermanes.

B. Ionization Energies of Oligogermanes

The structures of oligogermanes $Ge_n(CH_3)_{2n+2}$ with the regular all-trans form are fully optimized at the B3LYP/3-21G(d) level. Using the optimized structures, vertical ionization energies, denoted by EIP(ver), are calculated, and the results are plotted as a function of n in Figure 2. EIP(ver)'s for $n = 4$, 10, 20, and 28 are calculated to be 7.22, 6.08, 5.62, and 5.37 eV, respectively, indicating that EIP(ver)

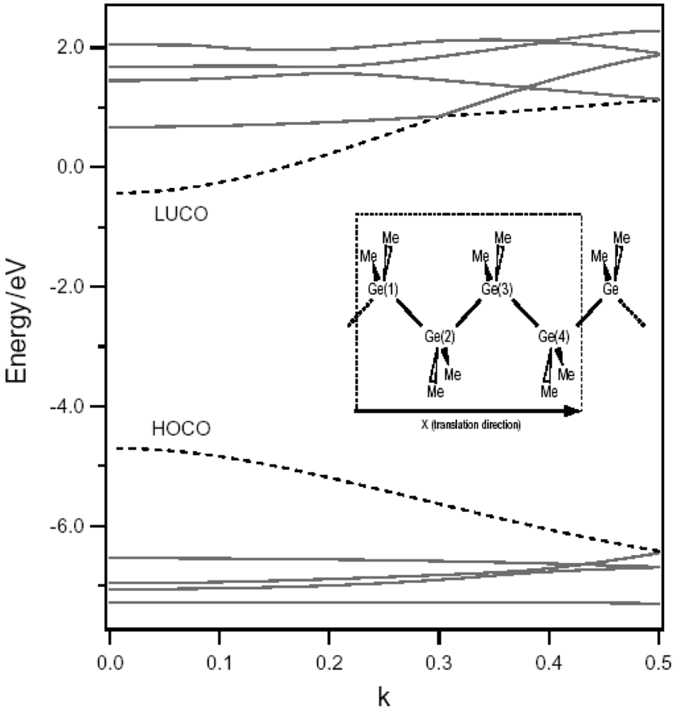

FIGURE 1 Band structure of poly(dimethylgermane) at neutral state calculated under the periodic boundary condition (B3LYP/3-21G(d) level). HOCO and LUCO mean highest occupied crystal orbital and lowest unoccupied crystal orbital, respectively.

TABLE 1 Optimized Geometrical Parameters Obtained for an Unit Cell of Poly(Dimethylgermane). The Unit Cell is Consisted of four Ge Atoms, Expressed by Ge(1)–Ge(2)–Ge(3)–Ge(4). Bond Lengths and Angles are in Å and in Degrees, Respectively

Parameters	HF/3-21G(d)	B3LYP/3-21G(d)
Ge(1)–Ge(2)	2.4351	2.4148
Ge(2)–Ge(3)	2.4410	2.4184
Ge(3)-Ge(4)	2.4351	2.4125
<Ge(1)–Ge(2)–Ge(3)	111.2	110.3
<Ge(2)–Ge(3)–Ge(4)	111.2	111.2
<Ge(1)–Ge(2)–Ge(3)–Ge(4)	157.3	158.8
Translation vector	7.9959	7.9067

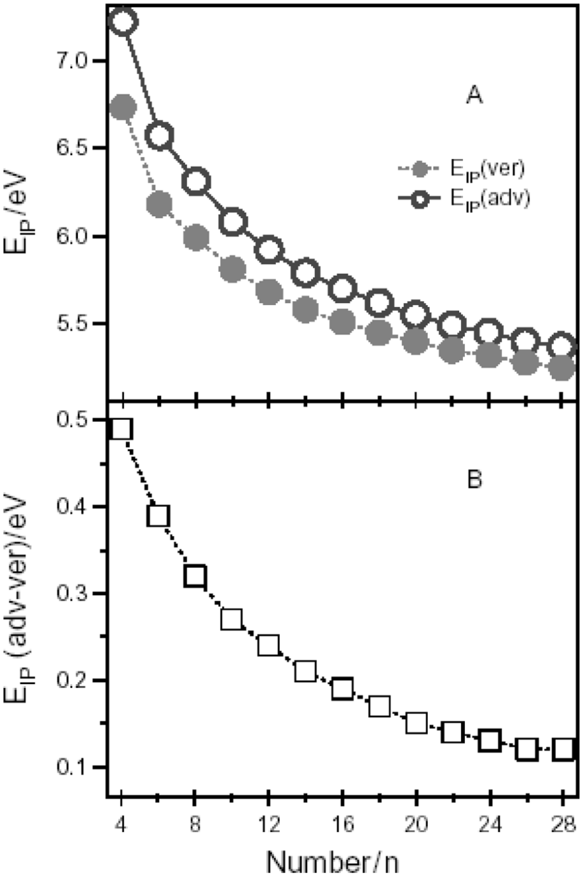

FIGURE 2 Vertical and adiabatic ionization energies of oligogermanes plotted as a function of chain length (n): (A) Vertical and adiabatic ionization energies and (B) difference between the vertical and adiabatic ionization energies.

decreases gradually with increasing n. Next, the structures are further optimized at cation state, and adiabatic ionization energies, denoted by EIP(adv), are calculated. The results are plotted in Figure 1(A). EIP(adv)'s for n = 4, 10, 20, and 28 are calculated to be 6.73, 5.81, 5.45 and 5.25 eV, respectively. The difference between EIP(ver) and EIP(adv) for n = 4, 10, 20, and 28 are 0.49, 0.27, 0.17, and 0.12 eV, respectively (Fig. 2(B)). This result implies that the structural change of cation state becomes smaller in longer chains.

C. Excitation Energies of Neutral and Cation of Oligogermanes

As stated in introduction, a low-lying excited state correlates strongly with the electron conductivity in organic semi-conductor. Hence, determination of the electronic structures at the excited states is important to elucidate the mechanism of electron and hole conductivities in oligogermanes. The first excitation energies of neutral and cation of oligogermanes are given in Figure 3 together with oscillator strengths. At the neutral state, the first electronic transitions for

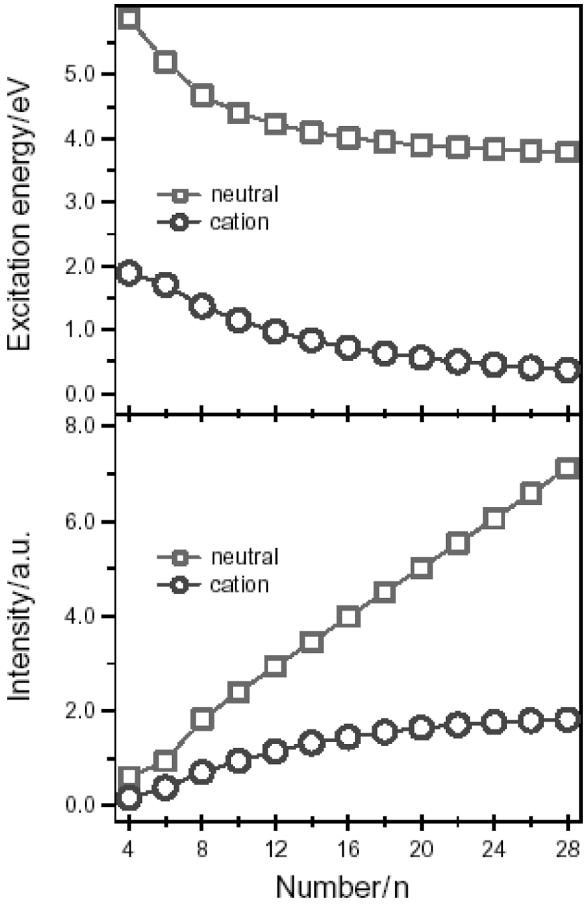

FIGURE 3 (A) First excitation energies of neutral and cation of oligogermanes plotted as a function of chain length, and (B) intensities of excitation energies (in arb. unit).

n = 4, 10, 20, 28 occur at 5.8, 4.4, 3.9 and 3.8 eV, respectively. The excitation energies decreased gradually with increasing chain length (n), and it reaches a limited value around n = 16. The oscillator strengths are linearly increased. The coefficient of the main configuration ϕ(HOMO→LUMO) is calculated to be 0.650 (n = 28) at the first excited state, and those of the other configurations are negligibly small, indicating that the excitation band is assigned to be the HOMO-LUMO transition of neutral oligogermane.

The radical cation has a significantly lower excitation energies. The excitation energies for the first electronic transitions in n = 4, 10, 20, 28 are calculated to be 1.9, 1.2, 0.6, 0.4 eV, respectively. For n = 28, the band gap is only 0.4 eV, which is low in energy enough to thermal hopping of hole along the Ge-Ge backbone. Thus, it can be summarized that band structure of oligogermane is significantly changed by doping of positive hole. The new energy bands are appeared at very low energy region below 0.5 eV. In particular, it is predicted theoretically that new energy band with a strong transition probability is generated at low energy region. This is an origin of hole transport in oligo- and polygermanes.

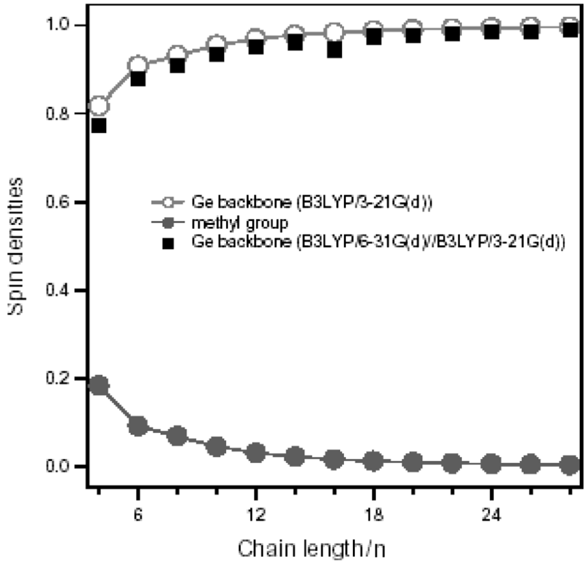

FIGURE 4 Spin densities on Ge-Ge backbone (main chain) and methyl group (side chain) plotted as a function of chain length (n).

D. Spin Densities

To elucidate distribution of unpaired electron in oligogermanes, spin densities on the Ge–Ge backbone (main chain) and the methyl group (side chain) are calculated at B3LYP/3-21G(d) and B3LYP/6-31G(d)//B3LYP/3-21G(d) levels of theory, and the results are given in Figure 4. Both calculations give the similar spin densities. For n = 4, the spin densities on the Ge–Ge backbone and methyl group are 0.82 and 0.18, calculated at B3LYP/3-21G(d) level. The spin densities on the Ge–Ge backbone increases with increasing n, and it becomes ca.1.0 above n = 10. Also, the spin densities on the side chain is close to zero. This result strongly implies that the hole is only localized in the Ge–Ge backbone, while the penetration of spin densities into the side chain is negligibly small in longer chain lengths.

CONCLUSION

The present calculations show that the hole is delocalized within the Ge–Ge skeleton, while the penetration of hole into the side-chain (methyl group) does not take place. In the case of polygermane with side-chain of alkyl groups, hole is delocalized along the Ge–Ge chain. Also, the band gap of oligogermane is significantly small in cationic state. Therefore, the hole is transferred along the Ge–Ge skeleton at thermal condition. Namely, in permethyl- oligogermanes and polygermanes, only intramolecular hole transfer is possible, but intermolecular hole transfer is significantly difficult. This is nature of hole transport in poly(dimethylgermane).

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