J. Phys. Chem. A **1999,** *103,* 2501−2505 **2501**

Electron Localization in Polysilane Radical Ions

Hiroto Tachikawa[†]

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8621, Japan

Received: September 16, 1998; In Final Form: January 12, 1999

The localization mechanism for the excess electron and positive hole in the polysilane radical anion and cation has been investigated by means of both molecular dynamics (MD) and extended Hückel molecular orbital (EHMO) calculations. A linear oligosilane (Si_nH_{2n+2}) ($n = 32$ and 64) was chosen as the model of polysilane. The geometry optimization of the polysilane at the MM2 level gave a regular all-trans form as the most stable structure. The MD calculations, started from the optimized structure, showed that the conformation of the polysilane skeleton was gradually randomized as a function of time by thermal activation at 300 K. The conformations at 0.0, 0.05, 1.0, 1.5, and 2.0 ps were chosen as sampling points, and spin densities on the silicon atoms were calculated by the EHMO calculations at each sampling point. An excess electron and a positive hole were fully delocalized along the Si chain in the regular all-trans form (time = 0.0 ps), whereas in the disordered conformations (time ≠ 0) both electron and hole were completely localized on a few Si atoms (10−20 monomer units). The present calculations suggested that a continuous disorder of the Si main chain randomized by thermal energy (i.e., disordered dihedral angle of Si skeletons) is dominant in both electron and hole localization. The localization mechanism was discussed on the basis of theoretical results.

1. Introduction

The localization and delocalization of the excess electron and positive hole along the polymer chain play an important role in the determination of its electronic properties because the localization correlates strongly with the electronic conductivity.[1,2] From a theoretical point of view, Tanaka et. al investigated the electron in polyacetylene by means of a simple Hückel model.[2] The oligomer composed of a 300-dimensional system was chosen as a model of the polyacetylene. The values of Coulomb (α) and resonance (*β*) integrals were randomly generated in order to express the random system. They concluded that the random arrangement of α and *β* values causes the electron localization in polyacetylene. Furthermore, they pointed out that the Anderson localization mechanism[1c] plays an important role in the electron localization in polyacetylene.

Polysilane is a one-dimensional *σ*-conjugated polymer and is very analogous to polyacetylene.[1,3] The *σ* electron of polysilanes is known to be strongly delocalized along a chain. However, recent experiments for charged polysilanes show that both the conduction electron and hole are localized in a few silicon atoms.[4,5] Irie et al. investigated the absorption spectra of radical ions of low molecular weight poly(methyl-*n*-propylsilane)s and pointed out that both excess electron and hole are localized on 16 silicon atoms of the main chain.[4] They examined chain length dependence on the absorption spectra of the anion and cation radicals. The spectra had two peaks in UV and near-infrared regions, and the maxima in both spectra shifted to longer wavelengths with increasing chain length until about 16 monomer units and showed saturation above this chain length.

The radical anion and cation of polysilanes were studied also by Ichikawa and co-workers.[5] They measured electron spin resonance (ESR) and absorption spectra of radical ions of poly(cyclohexamethylsilane) and concluded that the excess electron and hole are localized on a few silicon atoms (about six monomer units). Thus, the previous studies reported that the excess electron and hole on the polysilane radical ions are localized on a few silicon atoms, although the localization length is slightly different in each work.

Recently, we have investigated the structures and electronic states of the polysilane radical anions[6] and cations[7] by means of semiempirical PM3-CI calculations. The permethylated oligosilane [$Si_n(Me)_{2n+2}$] ($n = 8-20$) was chosen as a model of polysilane. We showed that the excess electron and hole are fully delocalized along the skeleton of linear polysilane if the structure has the regular all-trans form. The electronic excitation energy from the ground and 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 (hole) is not localized in the case of the regular all-trans form in the linear polysilane but is delocalized widely along the main chain.

In the present study, the theoretical calculations on the linear polysilane radical anion and cation have been carried out in order to shed light on the localization mechanism. The ordered and disordered structures of the Si skeleton in the oligosilane (i.e., all-trans and random forms, respectively) were considered. We focus our attention on the disordered dihedral angle of Si−Si−Si−Si activated by thermal energy.

2. Method of the Calculations

A linear oligosilane (Si_nH_{2n+2}) ($n = 32$ and 64) was chosen as a model of polysilane. First, the structure of the oligosilane was fully optimized by the MM2 method. From the fully optimized structure (i.e., the regular all-trans structure), molecular dynamics (MD) calculations were made at finite temperatures by using the potential energy and its gradient at the MM2 level structure, and the structure of the polymer was monitored as a function of time. We used 300 K for the simulation

[†] E-mail: hiroto@eng.hokudai.ac.jp. Fax: +81 11706-7897.

10.1021/jp983741j CCC: $18.00 © 1999 American Chemical Society
Published on Web 03/25/1999

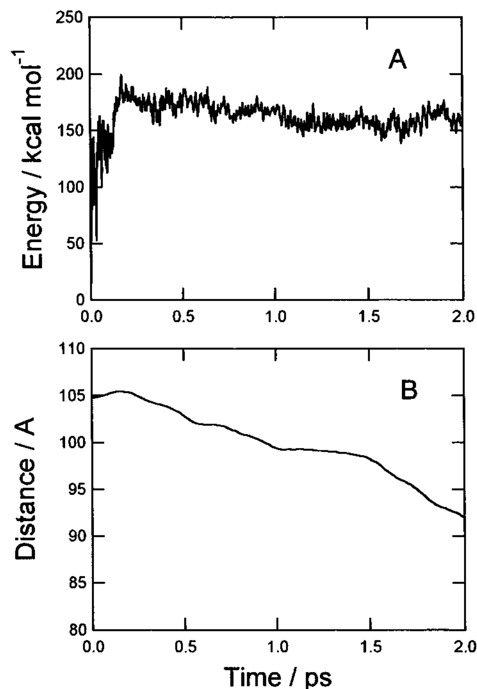

Figure 1. Potential energy (A) in kcal mol^{-1} and chain length in Å (B) (distance between head and tail of a chain) obtained by MM2-MD calculation at 300 K.

temperature throughout. The time step was 0.2 fs. The temperature is defined by

$$T = \frac{1}{3Nk}\langle\sum_{i=1}^{M} m_i v_i^2\rangle$$

where M is the number of atoms, v_i and m_i are the velocity and mass of the ith atom, and k is Boltzmann's constant. The conformations at 0.0, 0.05, 1.0, 1.5, and 2.0 ps were chosen as sampling geometries. The spin densities on the silicon skeleton were calculated by extended Hückel molecular orbital (EHMO) method using the structures generated by MM2-MD calculation. More details of the method for the dynamics calculation are described elsewhere.[8]

3. Results

A. Structures of the Model Polysilane at Finite Temperature. First, the structures of the model polysilane Si_nH_{2n+2} (n = 32 and 64) were fully optimized by the MM2 energy-gradient method. The regular all-trans form was obtained as the most stable form. Second, the molecular dynamics (MD) calculations was run at 300 K from the equilibrium structure. The result for $n = 32$ was essentially similar to that for $n = 64$ so that we will discuss here the result for $n = 64$. Figure 1 shows the result of the MD calculation for $n = 64$. The potential energy was almost constant. The chain length, defined by a distance between head and tail silicon atoms of the main chain, was varied as a function of time (Figure 1B). This result suggests that the structural conformation of the Si skeleton is gradually deformed and randomized by thermal activation. In particular, the dihedral angle, which is defined by the angle of the silicon skeletons Si(J)−Si(J + 1)−Si(J + 2)−Si(J + 3) (where J is a position of the Si atom), was largely varied as a function of simulation time. Figure 2 shows variation of the dihedral angles (ϕ) obtained by the MD calculations at 300 K. The structure has a regular all-trans form at time zero (Figure 2A). The

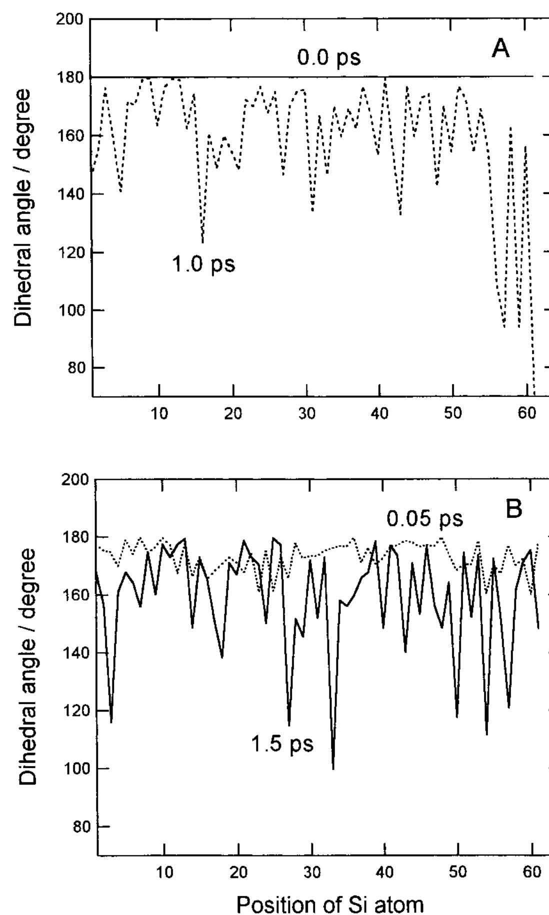

Figure 2. Distributions of dihedral angles (in deg) calculated as a function of simulation time.

dihedral angle was close to that of the regular all-trans form (ϕ = 180°). At 0.05 ps, despite a very short time propagation after thermal activation, the conformation of the linear chain was largely deformed (Figure 2B). The angle was distributed in the range ϕ = 160−180°. The distribution of the angle becomes more wide as ϕ = 120−180° at 1.00 ps. The large distorted site was located at the end of the chain (J = 50−60). At 1.50 ps, the angle was distributed in the range 100−180°. The largest distorted site was located in J = 20−35. The results for 2.00 ps was essentially similar to that for 1.50 ps.

B. Localization of the Excess Electron. The spin densities for an excess electron on the silicon chain (i.e., radical anion) were calculated by means of the extended Hückel molecular orbital (EHMO) method. The conformations of the polysilane at 0.0, 0.05, 1.00, and 1.50 ps were selected as sampling points. The calculated spin densities are given in Figure 3. The distributions of the spin densities were drastically changed as a function of time. At time zero the polymer has the regular all-trans form and an excess electron was completely delocalized along the polymer chain. After 0.05 ps, the distribution was significantly changed; the excess electron was localized on J = 28−42. This result suggests that the excess electron is localized in a few silicon atoms (14 silicon atoms). At 1.0 ps, the localization site was changed in J = 51−61, where the main chain is fully ordered. This site moved to J = 18−30 at 1.50 ps. By comparison of the results given in Figures 2 and 3, it can be concluded that the excess electron is preferentially localized in the disordered site composed of a few silicon atoms in the polymer chain.

C. Localization of Hole in the Polymer Chain. Similar calculations were carried out for a positive hole in the polysilane

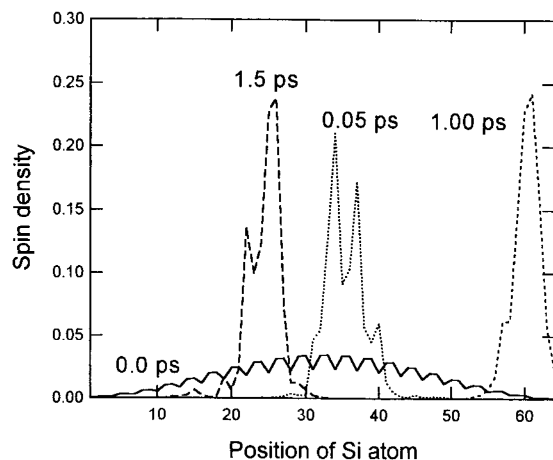

Figure 3. Spin densities for the excess electron in polysilane radical anion $[Si_nH_{2n+2}]^-$ ($n = 64$).

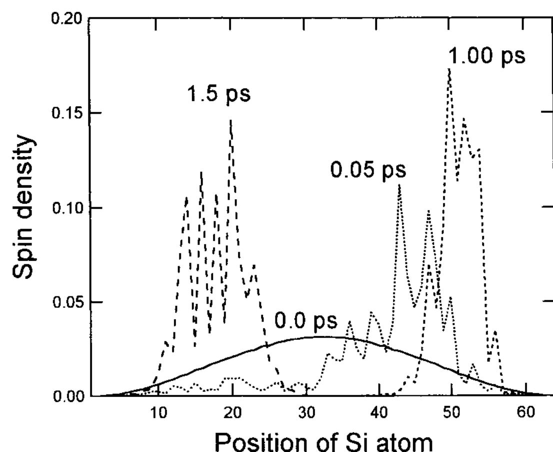

Figure 4. Spin densities for the positive hole in polysilane radical cation $[Si_nH_{2n+2}]^+$ ($n = 64$).

(i.e., radical cation). The spin densities on silicon atoms calculated by EHMO are given in Figure 4. The structural conformations of the polymer chain at the sampling points were the same as those of the radical anion. At the starting point of the dynamics calculation (time zero), a hole was fully delocalized along the polymer chain. This result is very similar to that obtained for the excess electron (Figure 3). At 0.05 ps, the positive hole was distributed in $J = 32-52$. It was found that the hole is localized on a few silicon atoms and that the localization site moves along the polymer chain as a function of time. The localization length of the hole is estimated to be $N = 9-25$. The feature that the hole is localized by the disordered dihedral angle of the polymer chain is very similar to that of the excess electron.

D. Electron and Hole Localization in the Defect in Polysilane. As mentioned above, both the hole and electron were localized in a continuous disorder distributed along the chain. In particular, the excess electron was preferentially localized on a specific disordered site in the polymer. On the other hand, it seems that a hole does not prefer that site but is localized by only a continuous disorder. To confirm these features in more detail, we have examined the calculations for the electron and hole in a polysilane having a specific distorted site (i.e., a lumped disorder in which segments of essentially perfectly ordered regions are separated by defects). The dihedral angles in the defect site ($J = 39-48$) were randomly generated in the range 100−180°. The angle for the other site in the polymer was fixed to 180° (i.e., the regular region). The results for the lumped disorder are given in Figure 5. In the case of this conformation, the dihedral angles in the defect were distributed in the range 150−120° (Figure 5A). EHMO calculations (Figure 5B) showed that the excess electron was localized in $J = 39-62$, whereas the hole was not localized in this region but was distributed in the ordered-structure site ($J = 1-40$). The other simulations using several conformations having the restricted disordered site gave similar results.

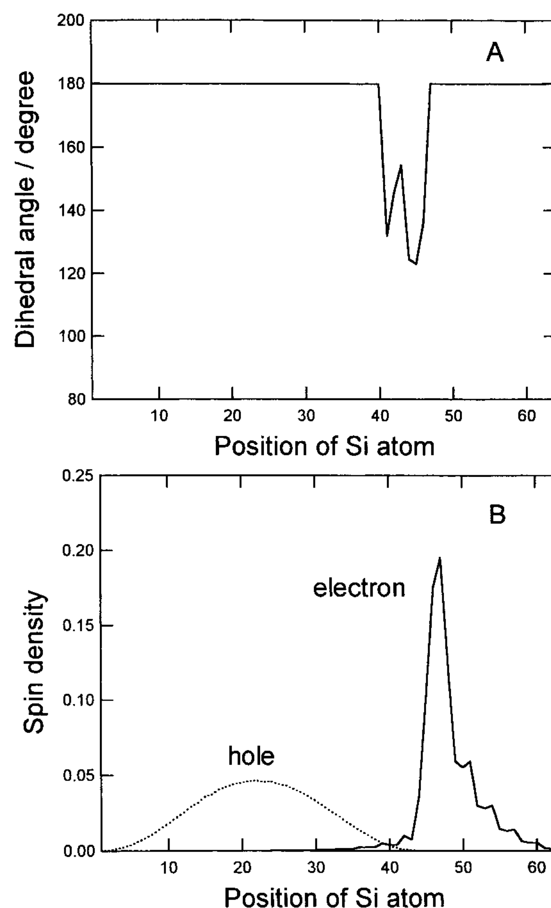

Figure 5. Electron and hole localization in the lumped disorder site in which segments of ordered regions are separated by defect: (A) distribution of dihedral angles (in deg); (B) spin densities for the excess electron and positive hole.

4. Discussion

A. Model of Electron and Hole Localization in Polysilane. In this study, we investigated the electronic states of charged polysilanes (anion and cation) by means of both MD and EHMO calculations. On the basis of the present results, we shall propose a model for the electron and hole localization in polysilanes. A model is illustrated in Figure 6 for a better understanding of the localization. An excess electron and a hole are fully delocalized over the entire main chain in the regular all-trans form (Figure 6, left), whereas in a continuous disorder of the main chain the electron and hole are localized in a few silicon atoms (Figure 6, central). It should be noted that the localization site of the hole is essentially different from that of the electron. In a lumped disorder, in which segments of essentially ordered regions are separated by a defect (Figure 6, right), an excess electron is preferentially localized in the defect site in the silicon chain. On the other hand, a hole is not localized in such a defect site but is delocalized in the ordered region (i.e., one of the segments). The hole is localized only in a continuous disorder.

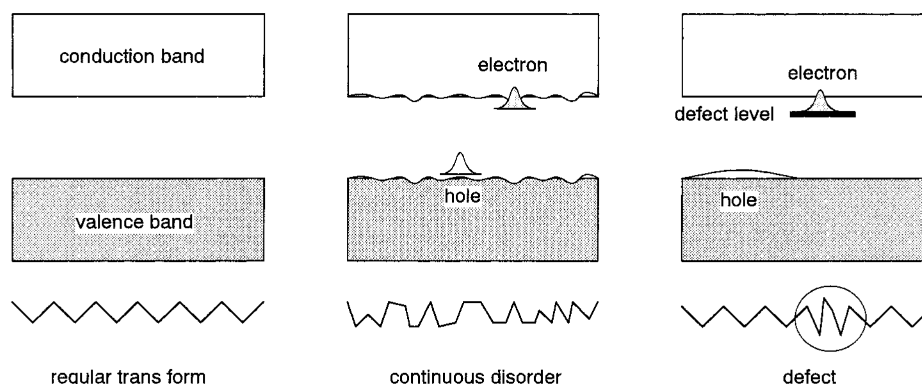

Figure 6. Schematic representation of the model for the electron and hole localization in polysilane.

B. Comparison with Previous Studies. The localization length of the conduction electron and positive hole in polysilanes (N) has been investigated by several groups. Irie et al. measured the electron absorption spectra of radical ions of various molecular weight poly(methyl-n-propylsilane)s in rigid matrices at 77 K.[4] The spectra had two peaks in UV and near-infrared regions, and the maxima of the peaks shifted to longer wavelengths with increasing chain length until about 16 monomer units and showed saturation above this length (i.e., $N = 16$). This reflects increasing electronic delocalization with increasing number of silicon atoms in the charged polymers.

Kumagai et al. measured electron spin resonance (ESR) and the electronic absorption spectra of oligosilane (Si_nR_{2n+2}, $n = 2-6$) and polysilane radical anions and cations.[5] The ESR spectra of the polymer radical ions are similar to those of the oligosilane radical ions. This suggested that both the excess electron and the hole in the polymer radical ions are not delocalized all over the Si−Si main chain. From an analysis of the ESR spectra, they concluded that the excess electron and hole in the polysilane radical ions are confined to only a part of the polymer chain composed of six atoms (i.e., $N = 6$). This length is much shorter than that determined by the experiment from the absorption saturation by Irie et al. ($N = 16$).[4]

The localization length of the electronic excitation has been also investigated. Tilgner et al. have shown that the excitation in poly(di-n-hexylsilane) is localized in a few tens of monomer units.[9] Thorne et al. have sought the conditions that need to be satisfied for excitation delocalization in σ-conjugated systems and found that at least 10 silicon atoms are required for a large polaron formation.[10] The present calculations indicate that both the electron and hole in the charged polysilanes are distributed in a few silicon atoms (about 10−20) in a continuous disorder along the chain. This feature agrees qualitatively with above experimental results.

The mechanism of the localization has been considered by several authors. Tilgner et al. investigated the electronic states of poy(di-n-hexyl-silane) in solid solution from both experimental and theoretical points of view.[9] They pointed out that the excitation is localized by a continuous disorder distributed along the chain. This model is very similar to the Anderson localization proposed for the electron localization in polyethylene.[2] Recently, Ichikawa et al. measured ESR spectra of oligo- and polysilane radical ions (Si_nR_{2n+2}, $n = 8$ and ∞).[13] By comparing the electronic states of oligo- and polysilanes, they implied that the Anderson localization may play an important role in the localization. The above experiments support strongly the present model.

Recently, mobilities of carriers along a chain were measured by the pulse-radiolysis method.[11] The mobility obtained for a positive hole was 3 times larger than that of the excess electron. This result may suggest that the localization mechanism of the hole and electron is different from each other. The excess electron is trapped in the defect of the main chain, as shown in Figure 6 (right), whereas the hole is not trapped, indicating that the mobility of the hole becomes larger than that of the excess electron. This may be the origin of the different electron conductivity.

The electron localization in one-dimensional polymers has been investigated theoretically by several groups, although almost all calculations were carried out for polyacetylene.[2,14] The previous theoretical calculations indicated that the bond alternation or a continuous disorder along the polymer chain causes the electron localization in a few carbon atoms. The present study indicated clearly that the continuous disorder of the polymer chain is the origin of the electron and hole localization mechanism in the charged polysilanes. This mechanism is very analogous to that of polyacetylene.

C. Concluding Remarks. We have introduced several approximations in calculating the electronic states and in treating the reaction dynamics. First, we assumed that the structures for the charged polysilanes are the same as that of neutral state. This assumption may cause a slight change of spin distribution in the polymer. However, the change may be minor because the structural change between neutral and ionic states is negligibly small, which was suggested by our previous papers[6,7] and experiments.[4,5]

Second, we used the EHMO method in calculating the spin densities. This level of theory is probably adequate to obtain the qualitative feature for electron and hole localization, which has been the subject of the present paper. However, a more accurate wave function is probably necessary for a reliable qualitative treatment (for example, spin density).[12] Despite the several assumptions introduced here, the results enable us to obtain valuable information on the mechanism of electron and hole localization in polysilanes. The present model presented here can explain reasonably the previous experiments.

Acknowledgment. The author is indebted to the Computer Center at the Institute for Molecular Science (IMS) for the use of the computing facilities. The author acknowledges partial support from a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

(1) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (c) Anderson, P. W. *Phys. Rev.* **1958**, *109*, 1492.

(2) Tanaka, K.; Nagaoka, M.; Yamabe, T. *Int. J. Quantum Chem.* **1983**, *23*, 1101.

(3) Trefonas, P., III: Djurovich, P. I.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.

(4) Irie, S.; Irie, M. *Macromolecules* **1997**, *30*, 7906.

(5) (a) Kumagai, J.; Yoshida, H.; Koizumi, K.; Ichikawa, T. *J. Phys. Chem.* **1994**, *98*, 13117. (b) Kumagai, J.; Yoshida, H.; Ichikawa, T. *J. Phys. Chem.* **1995**, *99*, 7965. (c) Kumagai, J.; Tachikawa, H.; Yoshida, H.; Ichikawa, T. *J. Phys. Chem.* **1996**, *100*, 16777.

(6) Tachikawa, H. *Chem. Phys. Lett.* **1997**, *265*, 455.

(7) Tachikawa, H. *Chem. Phys. Lett.* **1997**, *281*, 221.

(8) (a) Tachikawa, H. *J. Phys. Chem. A* **1998**, *102,* 7065. (b) Tachikawa, H.; Igarashi, M. *J. Phys. Chem. A* **1998**, *102,* 8648. (c) Tachikawa, H. *J. Phys. Chem. A* **1997**, *101*, 7475. (d) Program code of the direct dynamics calculation is created by our group.

(9) Tilgner, A.; Trommsdorf, H. P.; Zeigler, J. M.; Hochstrasser, R. M. *J. Chem. Phys*. **1992**, *96*, 781.

(10) Thorne, J. R. G.; Williams, S. A.; Hochstrasser, R. M.; Fagan, P. *Chem. Phys*. **1995**, *99*, 7965.

(11) van der Laan, G. P.; deHaas, M. P.; Hummel, A.; Frey, H.; Moller, M. *J. Phys. Chem.* **1996**, *102,* 5470.

(12) Semiempirical PM3 calculations on the electron and hole in $Si_{32}(CH_3)_{66}$ are now in progress in our group. A preliminary result was essentially similar to the results of the present calculations. Tachikawa, H.; Yamada, Y.; Ichikawa, T. To be published.

(13) Ichikawa, T.; Koizumi, K.; Kumagai, J. *J. Phys. Chem. B* **1997**, *101,* 10698.

(14) Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* **1992**, *114*, 2440.