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Ab Initio MO Studies on Polysilane Oligomer Radical Anions as Model Molecules of Polysilane Radical Anions

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Polysilane oligomer radical anions with up to six Si atoms have been theoretically investigated as model molecules of high polymer polysilane radical anions by ab initio MO theory. According to the calculated results, the polysilane oligomer radical anions can exist as bound anions having a σ-type ground state with an unpaired electron occupying a Si−Si antibonding σ^* orbital. They are stabilized with an increase in the Si−Si main chain length both in terms of the boundness of an unpaired electron and bonding strength. The π-type states, on the other hand, exist as excited states for these oligomer radical anions. The calculated results strongly suggest that polysilane radical anions with a π-type ground state are hardly generated regardless of their molecular size and geometry. The Si 3d orbital contributions in the ground and excited states of the polysilane radical anions, such as dπ−dπ conjugations, have also been investigated.

1. Introduction

Since the synthesis of organopolysilanes[1] which are soluble in conventional organic solvents, polysilanes have attracted considerable attention as so-called σ-conjugated polymers.[2] As is well-known, they have some unique properties, such as their fairly low-lying excited states,[3] nonlinear optical properties,[4,5] and their semiconducting and photoconducting properties,[6] as compared with the conventional polymers with carbon backbones. One of these properties is that relatively stable polymer radical anions are generated when polysilanes are exposed to ionizing radiation.[7−13] Generation of relatively stable polysilane oligomer radical anions has also been reported.[10,12] The lifetime of the aliphatic and aromatic linear polysilane radical anions in solution was reported to be in the range of 5−30 μs at room temperature.[9,11] On the contrary, such stable radical anions have not been observed for analogous aliphatic hydrocarbon polymers and oligomers. In previous papers,[14,15] we reported theoretical studies on the molecular and electronic structures of the disilane radical anion as a prototype of polysilane and its oligomer radical anions. In these studies, we have theoretically confirmed the following results. (1) The disilane radical anion can exist as a bound anion having a positive first vertical ionization potential (VIP) value. (2) It has a C_{2h} minimum energy geometry and a ^2B_u electronic state with an unpaired electron occupying a Si−Si σ^* antibonding orbital having a large s-type orbital coefficients, instead of a π type orbital. These results suggest that polysilane and its oligomer radical anions have the same kind of molecular and electronic structures with an unpaired electron occupying a Si−Si σ^* antibonding orbital. On the other hand, the resonance temporary anion states of polysilane oligomers were theoretically studied based on the stabilized KT (Koopmans theorem) approximation, reporting that the lowest energy unfilled MO of Si_nH_{2n+2} ($n > 2$) is largely SiH_2 σ^* in character.[16] This implies that their lowest unfilled MO is not a π-type orbital as far as they are at the equiribrium geometry of electrically neutral molecules. On the contrary, it has been reported that an unpaired electron of polysilane and its oligomer radical anions occupies an in-plane pseudo π-type orbital with no Si 3s orbital participation based on the electron spin resonance (ESR) study.[13] The semiempirical PM3 study[17] has also reported that an unpaired electron occupies an in-plane π^*(Si−Si) orbital for linear polysilane oligomer radical anions. These reported results are not consistent with our theoretical result that an unpaired electron of disilane radical anion occupies an Si−Si σ^* antibonding orbital with a large Si s-type orbital participation. Except for the case where an unpaired electron occupies a normal out-of-plane π-type orbital, it is unconceivable that the singly occupied molecular orbital (SOMO) has no or little Si 3s orbital participation, even in the case of relatively large linear polysilane radical anions, at least as far as they are at their minimum energy geometries. Our calculated SOMOs of the disilane radical anion and some related polysilane oligomer radical anions are far from the in-plane pseudo π-type orbitals.

On the other hand, the reported experimental result[13] that no Si^{29} hyperfine structure was found in the ESR spectra of the polysilane and its oligomer radical anions cannot deny the possibility that the SOMO consists of a normal out-of-plane π-type orbital. This discrepancy between our theoretical results and the ESR results puts forward the following possibilities. One is that the π-type state, initially in the excited state in the small size molecules, may be stabilized with an increase in the chain length and may come to be in the ground state in the case of long chain polysilanes. Considering that the polysilane radical anions observed by ESR spectroscopy are in the MTHF (2-methyl tetrahydrofuran) matrix environment at 77 K, they may not take their minimum energy geometries. So the other possibility is that the π-type state may come to be in the gorund state in a certain geometry formed in the MTHF matrix. These possibilities can be theoretically assessed by ab initio MO calculations.

On the basis of these results, we have carried out detailed theoretical studies on polysilane oligomer radical anions having up to six silicon atoms ($Si_2H_6^-$, $Si_3H_8^-$, $Si_4H_{10}^-$, $Si_5H_{12}^-$,

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and $Si_6H_{14}^-$) as model molecules of linear polysilane radical anions. In this paper, our attention has been focused mainly on the following aspects. 1. What kind of molecular and electronic structures do the polysilane and its oligomer radical anions have in their ground states? 2. To what extent are their molecular properties affected by their molecular size? 3. Is there any possibility that the π-type state can exist among polysilane and its oligomer radical anions in their ground states? In other words, what kind of π-type states can exist in their ground and excited states?

2. Method of Calculation

Ab initio MO calculations on the ground state of the polysilane oligomer radical anions were performed in a manner analogous to the previously reported calculations.[15] The minimum energy geometries were initially optimized at the Hartree−Fock level and were confirmed by harmonic vibrational frequency analyses. They were further reoptimized by the MP2[18,19] level calculations. Energy quantities, such as the first VIP and adiabatic electron affinity (EA), were estimated by the MP4SDTQ[18,19] level calculations at the MP2 optimized geometries. The wave functions in the ground state were confirmed to be dominated by the Hartree−Fock determinant by CISD calculations. The calculated $\langle S^2 \rangle$ values of the UHF wave functions for the radical anions are in the range of 0.75−0.79, indicating that there exists no serious spin contamination in our UHF and UHF based post-Hartree−Fock level calculations. Charge distributions were estimated on the basis of the Mulliken population analyses[20,21] using the MP2 wave functions.

We employed the same double-ζ quality basis set as employed in the previous paper.[15] For Si and H atoms, Dunning−Huzinaga[22] (11s7p/6s4p) and (4s/2s) were employed, respectively. One set of d-polarization functions with an exponent of $\alpha_d(Si) = 0.5$ and one set of p-polarization functions with the exponent of $\alpha_p(H) = 1.0$ were added to the (11s7p/6s4p) and (4s/2s), respectively. For the Si atom, a single s and one set of p diffuse functions with the exponent of $\alpha_s(Si) = 0.029$ and $\alpha_p(Si) = 0.030$[15] were added to the double-ζ quality basis set. This basis set is denoted as DZPD as in the previous paper.[15]

The excited states of the polysilane oligomer radical anions were calculated mainly at the simple CIS level of theory. In this case, all occupied and virtual orbitals except for core electron orbitals were included in the CIS active space. A part of the CIS results was compared with the excitation energies calculated by other more rigorous theoretical approaches including the recently developed time-dependent DFT (TDDFT)[23,24] approach and was confirmed by the most rigorous MRMP[25] calculations, which were reported to provide quantitatively reliable results.[26−28]

In the TDDFT calculations, the B3LYP[29] and PBE0[30] hybrid exchange-correlation functionals were employed. Because the excited wave functions in the relatively low-lying levels were confirmed to be dominated by singly excited configurations based on our CISD calculations, even the CIS level calculations are expected to provide qualitatively the same results as those calculated by the more rigorous approaches. In addition to the DZPD basis set, the DZPD1 and DZPD2 were employed for calculations of excited states. In the DZPD1 basis set, one set of d functions was added to the DZPD of Si atom to study the dπ−dπ conjugation effect on the stability of the π-type states. This DZPD1 basis set was also employed to study the diffuse Si 3d orbital contribution in the ground state of the oligomer radical anions. Rydberg s, p, and d functions ($\alpha_s(Si) = 0.012$, $\alpha_p(Si) = 0.015$, and $\alpha_d(Si) = 0.014$)[31] were added to the DZPD set to form the DZPD2 basis set. The latter basis set was employed to study the excited states of the polysilane oligomer radical anions in the gas-phase environment. The Gaussian 92[32], 98[33] and HONDO 95[34] programs were employed for both the ground state and excited state calculations. The MR2D[35] program was employed for the MRMP calculations where state-averaged CASSCF functions were used as reference ones.

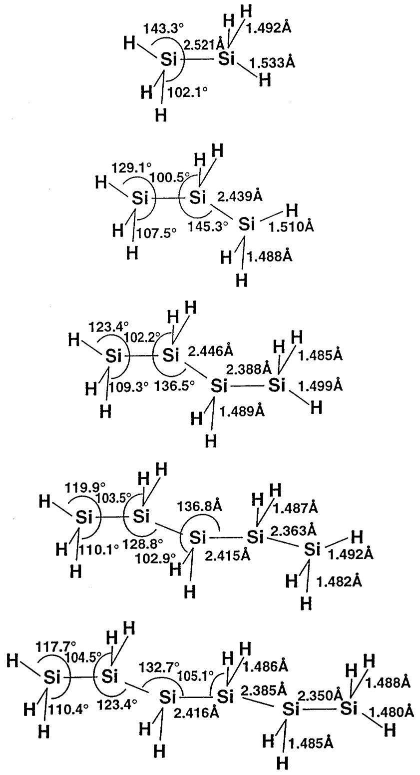

Figure 1. Calculated minimum energy geometries of the five polysilane oligomer radical anions (UMP2/DZPD).

TABLE 1: Calculated Molecular Properties of Polysilane Oligomer Radical Anions (MP4SDTQ/DZPD//MP2/DZPD)[a]

molecules	EA (eV)	first VIP (eV)	$r(\overline{Si-Si})^a$ (Å)	symmetry	
$Si_2H_6^-$	−1.218	0.152	2.521	C_{2h}	^2B_u
$Si_3H_8^-$	−0.756	0.377	2.439	C_{2v}	$^2A_1$
$Si_4H_{10}^-$	−0.460	0.515	2.407	C_{2h}	^2B_u
$Si_5H_{12}^-$	−0.256	0.607	2.389	C_{2v}	$^2A_1$
$Si_6H_{14}^-$	−0.103	0.674	2.377	C_{2h}	^2B_u

[a] $r(\overline{Si-Si})$: Averaged Si−Si bond distance of a polysilane oligomer radical anion.

3. Electronic Structures and Molecular Properties of the Polysilane Oligomer Radical Anions in Their Ground State

Calculated minimum energy geometries of the polysilane oligomer radical anions are summarized in Figure 1. Symmetries for their structures and electronic states are also summarized in Table 1 together with their molecular properties. As shown in Figure 1 and Table 1, they have two kinds of molecular and electronic structures. Although the oligomer radical anions containing an even number of Si atoms have C_{2h} minimum energy geometries and a ^2B_u electronic state, those with an odd number of Si atoms have C_{2v} minimum energy geometries and an $^2A_1$ electronic state. Despite these different symmetries for the molecular and electronic structures, they have similar electronic states with an unpaired electron occupying a main chain Si−Si σ***** antibonding orbital, instead of a π-type one. Their singly occupied molecular orbitals (SOMOs) consist of a large Si s-type orbital contribution as well as a p-type orbital contribution. Namely, they have molecular and electronic structures that are similar to those of the disilane radical anion, suggested in the previous papers,[14,15] which is clearly inconsistent with the reported experimental[13] and theoretical[17] results.

As shown in Figure 1, these oligomers receive the same kind of distortion when they receive an electron. These radical anions are stabilized with an increase in the Si−Si bond distance and Si−Si−Si and Si−Si−H bond angles. In the case of Si_6H_{14}, for example, the central Si−Si−Si bond angle is increased from 112.6 to 132.7° and the central Si−Si bond distance is increased from 2.330 to 2.416 Å. This change in bond distance is due to the Si−Si antibonding character of the SOMO. It should be also noticed that the Si−Si bond distances of the oligomer radical anions are incresed from the end to the center of the Si chain. The Si−Si bond distance is increased from 2.350 to 2.416 Å as the bond position is shifted from the end to the center part, in the case of the Si_6H_{14} radical anion, for example. This marked geometrical trend is not found in the neutral polysilanes and their oligomers. This is due to the fact that the SOMO density on the Si−Si main chain is increased from the end to the center part of the chain. As a result, the SOMO has the largest antibonding character on the central Si−Si bond. The calculated total overlap populations of the Si−Si bonds in the Si_6H_{14} radical anion are decreased in the order of −0.506, −2.144, and −4.944 as the bond position is shifted from the end to the center part. Thus, the change in Si−Si bond distance on the main chain is reflected by this SOMO density variation on the main chain of the oligomer radical anions.

The stability of these polysilane oligomer radical anions can be estimated by the stability of an unpaired electron and the bonding strength. Table 1 indicates the calculated first vertical ionization potential (VIP) and averaged Si−Si bond distance (r(Si−Si)) values for the oligomer radical anions together with their symmetries for the molecular and electronic structures. The calculated adiabatic electron affinity (EA) values of the neutral oligomers are also summarized in Table 1. This is because the adiabatic EA value is also closely associated with the stability of the radical anions.

As indicated in Table 1, the oligomer radical anions have negative adiabatic EA and positive first VIP values, meaning that they are bound anions although the neutral oligomers are destabilized by receiving an electron. So the calculated results indicate that all of these oligomer radical anions can exist as bound anions. Although these radical anions have not been reported to be experimentally observed, methyl substituted tetrasilane, pentasilane, and hexasilane oligomer radical anions have already been reported to be experimentally observed,[12,13] which is consistent with our calculated results. Second, a marked molecular size effect can be seen in Table 1. The adiabatic EA and first VIP values are increased with an increase in the Si main chain length. The first VIP value, for example, is increased from 0.152 to 0.674 eV as the size of the radical anion goes up from $Si_2H_6^-$ to $Si_6H_{14}^-$. This indicates that an unpaired electron becomes more tightly bound with an increase in the Si main chain length, meaning that the oligomer radical anion is stabilized with an increase in the molecular size. This stability change is reflected in the diffuse orbital participation in the SOMO. Although the s-diffuse function coefficients in the SOMO of the Si_2H_6 radical anion have a value of 0.45 in the case of an UHF wave function, those of the Si_6H_{14} radical anion have values of 0.03, −0.12, and 0.29 in order from the end to the center Si atom. Namely, diffuse orbital participation is decreased with an increase in the molecular size. This also shows that an unpaired electron in the oligomer radical anions is stabilized with an increase in the molecular size. In Table 1, it should also be noted that the averaged Si−Si bond distance is decreased with an increase in the molecular size. In other words, the Si−Si bonding strength of the oligomer radical anions is enhanced with an increase in the molecular size. So the polysilane oligomer radical anions are stabilized both in terms of the boundness of an unpaired electron and the main chain bonding strength with an increase in the main chain length, meaning that it becomes correspondingly easier to experimentally observe the polysilane radical anions including the oligomer anions according as the molecular size is increased.

In the previous papers,[14,15] we reported that no Si 3d orbital participation is found in the Si_2H_6 radical anion. In this paper, we have also studied the possibility of the Si 3d orbital participation in the polysilane oligomer radical anions in their ground state. This is because a Si 3d orbital contribution has been suggested for a cyclic polysilane radical anion.[36,37]

To study the diffuse Si 3d orbital participation in the polysilane oligomer radical anions, molecular wave functions were recalculated at their minimum energy geometries by using the DZPD1 (DZPD plus one set of d functions) basis set. In the second Si d orbital exponent range from 0.01 to 0.5, little d orbital participation is found in the SOMO of the oligomer radical anions. Moreover, the optimized d orbital exponent for the oligomer radical anions has only values corresponding to those of polarization functions instead of the diffuse Si 3d orbitals. In the case of the Si_6H_{14} radical anion, for example, the optimized exponent has a value of 0.18 in the UMP2 level calculations. So the second d functions act as polarization functions as do the first d functions.

These calculated results clearly indicate that there exists no Si 3d orbital contribution in the ground state of the polysilane oligomer radical anions. This strongly suggests that there also exists no Si 3d orbital contribution in high polymer polysilane radical anions, at least as far as linear polysilane radical anions are concerned. In this respect, our calculated results are consistent with the reported small g-value anisotropy of ESR spectra interpreted as those of polysilane and its oligomer radical anions.[13]

Because our calculated result is not consistent with the reported PM3 result,[17] we have also calculated the polysilane oligomer radical anions by the semiempirical PM3 level of theory. According to our calculated results, the PM3 result is found to be completely different from the ab initio result. In the case of the Si_2H_6 radical anion, for example, although the ab initio calculation gives a C_{2h} minimum energy geometry with an increased Si−Si bond length due to the antibonding character of the SOMO, the PM3 calculation gives a D_{3d} one with a decreased Si−Si bond length which is similar to that of the neutral Si_2H_6 geometry. The large structural distortion[14,15] found in the ab initio calculations is not found in the case of the PM3 level calculation when the Si_2H_6 receives an electron. The same difference is also found for the Si_6H_{14} radical anion between the ab initio and the semiempirical PM3 results. Although the PM3 calculation gives a C_{2h} minimum energy geometry with an unpaired electron occupying a Si−Si σ***** antibonding orbital, its geometry is very close to the neutral molecule geometry. In this case, the Si−Si bond length is decreased by receiving an electron except for the end part of the Si−Si bonds in contrast to the ab initio result. These results indicate that the semiem-

TABLE 2: Calculated Vertical Excitation Energy for the Si_2H_6 Radical Anion Using the DZPD Basis Set at the UMP2/DZPD Geometry

excited states	symmetry	excitation energy (eV) CIS	CASSCF	MRMP	TDDFT B3LYP	TDDFT PBE0
first	^2A_g	2.00	1.34	1.70	1.58	1.66
second	^2B_u	2.43	1.70	2.18	1.95	2.04
third	^2A_u	2.67	1.88	2.44	2.34	2.43
fourth	^2A_g	2.77	2.12	2.63	2.36	2.43
fifth	^2B_u	2.84	2.26	2.63	2.52	2.57

TABLE 3: Calculated Vertical Excitation Energy for the Si_3H_8 Radical Anion Using the DZPD Basis Set at the UMP2/DZPD Geometry

excited states	symmetry	Excitation energy (eV) CIS	CASSCF	MRMP	TDDFT B3LYP	TDDFT PBE0
first	$^2A_1$	2.16	1.42	1.85	1.77	1.86
second	$^2B_2$	2.43	1.54	2.10	1.74	1.87
third	$^2B_1$	2.75	1.84	2.53	2.41	2.51
fourth	$^2A_1$	2.79	1.86	2.55	2.20	2.31
fifth	$^2A_1$	2.86	2.06	2.61	2.45	2.55

pirical PM3 level calculations fail to reproduce the ab initio results for the polysilane oligomer radical anions. Considering that the present PM3 level of theory is not parametrized to be particularly fit for anionic molecular systems, PM3 calculated results for anionic molecular systems are highly questionable.

4. Excited States of the Polysilane Oligomer Radical Anions

There exist π states in the excited states of polysilane and its oligomer radical anions, even though they have a σ ground state. The excited σ and π states are energetically stabilized with an increase in the Si−Si main chain length. If this stabilizing effect on the excited π state were larger than that of the σ states, there would be a possibility of the energy level of a certain π state, which is an excited one in the case of small size polysilane radical anions, being lower than the energy levels of the σ states. Thus, this π state, instead of the σ one, comes to be the ground state in the case of large polysilane radical anions. In this case, polysilane radical anions with an unpaired electron occupying a π-type orbital could be observed. On the other hand, reported experimental results have always been observed in the condensed phase, such as in the MTHF matrix environment. So there is a possibility that the dominant geometries of the polysilane and its oligomer radical anions in the condensed phase are different from those in the gas phase where molecules easily obtain their minimum energy geometries. If the excited π state were to be stabilized and allowed to become a ground state by a certain geometrical change, there may also be a possibility that polysilane radical anions with a π ground state could be experimentally observed in the condensed phase. To theoretically investigate these possibilities, we have studied the excited states of the polysilane oligomer radical anions mainly by the CIS level calculations.

To assess the reliability of the CIS level calculations on the polysilane oligomer radical anions, the vertical excitation energy and excited energy level ordering calculated by the CIS level of theory have been compared with those calculated by the more rigorous CASSCF, MRMP, and recently developed TDDFT approaches for the relatively small polysilane oligomer radical anions, $Si_2H_6^-$ and $Si_3H_8^-$. The calculated vertical excitation energies of the Si_2H_6 and Si_3H_8 radical anions using the DZPD basis set at the UMP2/DZPD ground state geometries are summarized in Tables 2 and 3, respectively. The five lowest excited states of the Si_2H_6 radical anion are the ^2A_g, ^2B_u, ^2A_u, ^2A_g, and ^2B_u states. In other words, the lowest π state of the Si_2H_6 radical anion is the third excited state (^2A_u). On the other hand, the five lowest excited states of the Si_3H_8 radical anion are the $^2A_1$, $^2B_2$, $^2B_1$, $^2A_1$, and $^2A_1$ states. So this oligomer radical anion also has the lowest π state as the third excited state ($^2B_1$).

Among the ab initio approaches of CIS, CASSCF, and MRMP, the state-averaged CASSCF calculations provide the lowest excitation energies among the three kinds of calculated values in these cases. The most rigorous MRMP calculations, in which both dynamical and nondynamical electron correlation effects are taken into consideration, provide intermediate values between the CIS and CASSCF calculated values. The CIS calculations, in which no dynamical electron correlation effect is taken into consideration, provide the highest excitation energy values. Considering that the most rigorous MRMP approach gives quantitatively fairly exact excitation energies,[26−28] it is considered that the CIS approach overestimates the excitation energy, whereas the CASSCF approach underestimates it in the case of our calculations on these oligomer radical anions.

However, it should be noted that the CIS approach reproduces the same excited energy level ordering as that calculated by the most rigorous MRMP approach. Concerning the excitation energies, the CIS level calculations consistently give values 1.1−1.2 times higher than those calculated by the MRMP approach in this case. We have also confirmed that singly excited configurations dominate the excited wave functions of the polysilane oligomer radical anions by our CISD calculations, indicating that even the CIS approach can be a fairly good approximation in estimating vertical excitation energies of the polysilane radical anions.

In the case of the TDDFT approach, on the other hand, while the TDDFT(PBE0) calculations give excitation energies fairly close to the most rigorous MRMP results, the TDDFT(B3LYP) calculations give relatively low excitation energies and a fairly different excited energy level order for the Si_3H_8 radical anion in comparison with the MRMP and TDDFT(PBE0) results, as shown in Table 3. As to the excited energy level ordering, even the TDDFT(PBE0) calculations fail to reproduce the MRMP results. In this case, the third and fourth excited states order is reversed for the Si_3H_8 radical anion as compared with the MRMP and other ab initio results. These results are consistent with the reported result[38,39] that the TDDFT(PBE0) calculations provide more accurate excitation energies and excitation energy level ordering than what the TDDFT(B3LYP) calculations give. Concerning the reported results,[39] even the TDDFT(PBE0) calculations give an excited energy level ordering which is partly different from that calculated by the more rigorous CASPT2[40,41] approach in some cases. In general, calculated excitation energies and excited energy level ordering are sensitive to the employed exchange-correlation energy functionals.[39] In this respect, the TDDFT approach should be carefully employed.

These results indicate that even the CIS level calculations provide fairly reliable results for the polysilane oligomer radical anions, at least from a qualitative point of view, despite the crude approximation. The excited energy level ordering between the σ- and π-type states of the oligomer radical anions, for example, can be fully estimated by the CIS level calculations. Moreover, geometry optimizations using the analytical energy derivative can be carried out in the CIS approach. We thus go on to investigate their excited states by the CIS level of theory.

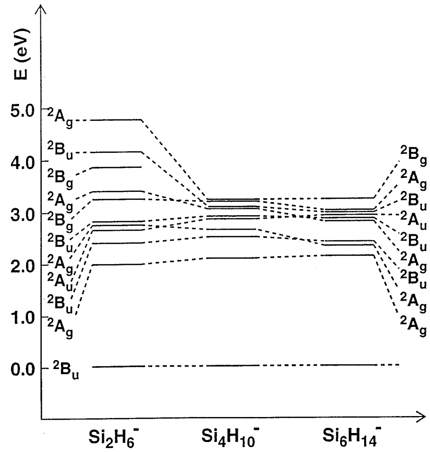

Figure 2. Molecular size effects on the excited energy levels of the polysilane oligomer radical anions with even numbers of Si atoms ($Si_2H_6^-$, $Si_4H_{10}^-$, and $Si_6H_{14}^-$) estimated by the CIS/DZPD//UMP2/DZPD level calculations.

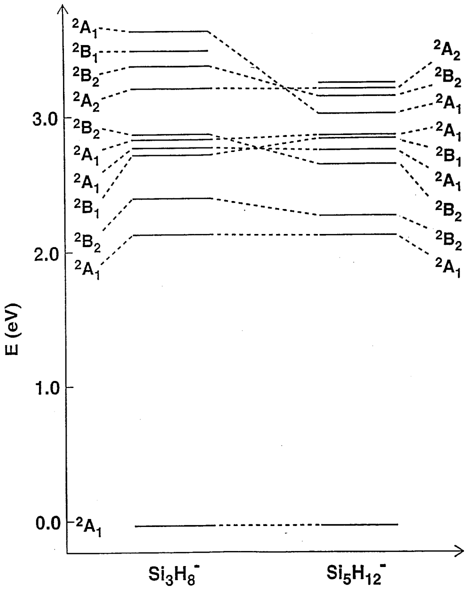

Figure 3. Molecular size effects on the excited energy levels of the polysilane oligomer radical anions with odd numbers of Si atoms ($Si_3H_8^-$ and $Si_5H_{12}^-$) estimated by the CIS/DZPD//UMP2/DZPD level calculations.

Figure 2 shows molecular size effects on the excited energy levels of the polysilane oligomer radical anions with C_{2h} symmetry ($Si_2H_6^-$, $Si_4H_{10}^-$, and $Si_6H_{14}^-$) estimated by the CIS level calculations. In Figure 2, it should be noted that more than half of the excited σ states (^2A_g and ^2B_u) are energetically stabilized with an increase in chain length, whereas the excited π state (^2A_u and ^2B_g) levels are not so much affected by chain length. For example, the ^2A_g states are steadily stabilized except for the first ^2A_g state. This leads to enhancement of the excited π state ordering with an increase in the chain length. The lowest excited π states for the Si_2H_6, Si_4H_{10}, and Si_6H_{14} radical anions are the third, fourth, and sixth excited states, respectively. Figure 3 also shows the same molecular size effects on the radical anions with C_{2v} symmetry ($Si_3H_8^-$ and $Si_5H_{12}^-$). The same trend in the σ and π excited states is also found in these radical anions. All of the $^2B_2$ and one $^2A_1$ excited states are energetically stabilized with an increase in chain length, whereas the excited $^2A_2$ and $^2B_1$ state levels are not so much affected. As a result, although the lowest excited π state is the third excited state in the Si_3H_8 radical anion, that of the Si_5H_{12} radical anion comes to be the fifth excited state. So the calculated results indicate that the excited π state level ordering for these oligomer radical anions is not lowered but rather enhanced as the main chain length is increased, strongly suggesting that there also exists the same trend for the polysilane radical anions of larger molecular size. From this point of view, it is unlikely that the π-type state would become a ground state in polysilane radical anions of large molecular size.

As shown in Figures 2 and 3, a few low-lying excited states are found to be somewhat enhanced with an increse in main chain length. This kind of tendency is not found in the neutral polysilane oligomers. Their excited states are steadily stabilized with an increase in main chain length. This peculiar tendency found in the oligomer radical anions strongly depends on the employed basis set and the geometry of the radical anions. In cases where the DZP basis set with no Si s and p diffuse functions is employed for the CIS calculations of the oligomer radical anions, no such peculiar tendency is found. In this case, the calculated excited states are steadily stabilized with an increase in main chain length. In other words, such peculiar tendency strongly depends on the diffuseness of the excited state wave functions in the case of the oligomer radical anions. It also depends on the geometry of the radical anions. In cases where the CIS calculations are carried out for the oligomer radical anions at the neutral geometries, the calculated excited states, except for one state, are found to be stabilized with an increase in main chain length.

As mentioned in the previous section, the minimum energy geometry of the polysilane oligomer is distorted when they receive an electron. The extent of this distortion is increased with a decrease in main chain length. This distortion difference among the oligomer radical anions is considered to be one origin of that peculiar tendency found in the calculated excited levels. Despite this peculiar tendency, it should be stressed that the excited energy levels with large oscillator strength are steadily stabilized with an increase in the main chain length. For example, the second ^2A_g state with large oscillator strength is steadily stabilized from the $Si_2H_6^-$ to $Si_6H_{14}^-$.

As previously mentioned, there exists a possibility that the σ-type electronic state of polysilane and its oligomer radical anions in their minimum energy geometries is changed to be a π-type state as a result of certain structural changes in the condensed phase. To assess this possibility, the geometries of the oligomer radical anions have been energetically optimized for their lowest π state instead of the σ state within the CIS level of theory. The calculated results indicate that the vertical excitation energy strongly depends on the structure of the oligomer radical anions. Figure 4 shows the change in excited energy levels of the Si_2H_6 radical anion when the geometry is changed from the minimum energy state of the ^2B_u ground state to that of the lowest π state (^2A_u). This figure indicates that excited energy levels, including the σ and π states, are considerably reduced by this geometrical change. This considerable lowering of the excited energy levels is also found in the remaining polysilane oligomer radical anions. This suggests that unexpectedly long wavelength optical absorption could be observed for polysilane and its oligomer radical anions in the condensed phase. Although the first ^2A_u π-type state is changed from the third to second excited state by this structural change, it should be noted that the Si_2H_6 radical anion still has the ^2B_u σ-type ground state. The same is also true of the remaining oligomer radical anions. Figure 5 shows the excited energy levels of the Si_2H_6, Si_4H_{10}, and Si_6H_{14} radical anions in cases where their geometries are energetically optimized for their

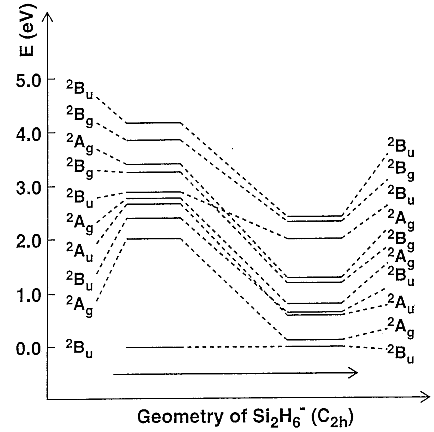

Figure 4. Excited energy levels change of the Si_2H_6 radical anion when the geometry is changed from the minimum energy state of the ^2B_u ground state to that of the lowest π state (^2A_u) estimated by the CIS/DZPD level calculations.

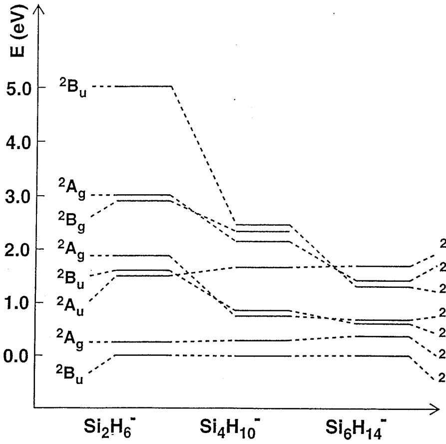

Figure 5. Calculated excited energy levels of the Si_2H_6, Si_4H_{10}, and Si_6H_{14} radical anions in cases where their geomtries are energetically optimized for their lowest π states (CIS/DZPD//CIS/DZPD).

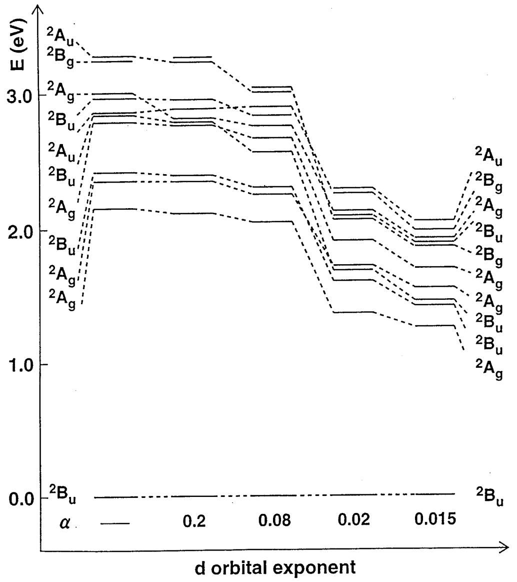

Figure 6. Excited energy levels change of the Si_6H_{14} radical anion when the second Si d orbital exponent is varied from 0.2 to 0.015 estimated by the CIS/DZPD//UMP2/DZPD level calculations.

lowest π states. As shown in Figures 2 and 5, the ordering of the lowest π states of the Si_4H_{10} and Si_6H_{14} radical anions is rather enhanced after the geometrical change. The lowest π state ordering is also enhanced with an increase in Si main chain length in this case, whereas excited energy levels are considerably lowered as compared with those shown in Figure 2. These calculated results, therefore, deny the possibility that polysilane oligomer radical anions having a π-type ground state are formed by a certain structural change by a cage effect in the condensed phase. We suggest that the same thing can be said for polysilane radical anions of large molecular size.

In the previous section, we have theoretically confirmed that there exists no Si 3d orbital contribution in the ground state of the polysilane oligomer radical anions. On the other hand, Si 3d orbital participation, such as dπ−dπ conjugations, has often been suggested in the excited states of Si-containing molecular systems.[42−44] In addition to the pπ−pπ conjugations, the dπ−dπ conjugations are naturally expected in the π states of the polysilane and its oligomer radical anions. To investigate this possibility, the excited π states of polysilane oligomer radical anions were calculated by using the DZPD1 basis set with various d orbital exponent values. Figure 6 shows the changes in excited energy levels for Si_6H_{14} radical anion when the second d orbital exponent is varied from 0.2 to 0.015. This figure indicates that the calculated excitation energies, including the σ and π states, are seriously affected by the d orbital exponent. With a d orbital exponent value of less than 0.08, the excitation energy values are considerably reduced and the lowest π state are changed from the ^2A_u to the ^2B_g state in this case. Marked dr−dx conjugations are generated in the π states of the Si_6H_{14} radical anion in this diffuse d-orbital exponent region, which leads to considerable lowering of the calculated excitation energy values. Although it is rather difficult to theoretically estimate excited states in the condenced phase, these calculated results suggest a possibility of dπ−dπ conjugations in the excited π states of polysilane and its oligomer radical anions. It should also be noted that the excited π state energy level ordering is not lowered by the generation of large dπ−dπ conjugations despite the excited energy level lowering. This denies the possibility that the π state becomes a ground state of the polysilane oligomer radical anions due to dπ−dπ conjugations.

However, the DZPD1 basis set is not a well balanced basis set for calculations of excited states. This is because it includes only the diffuse d functions for the excited states. To properly estimate the excited states of the polysilane oligomer radical anions in the gas phase, the CIS level calculations were carried out by using the DZPD2 basis set containing Si Rydberg s, p, and d functions. Figure 7 compares the vertical excitation energy levels calculated by the DZPD basis set with those calculated by the DZPD2 basis set in the case of the Si_4H_{10} radical anion. As shown in Figure 7, the calculated excited energy levels are considerably reduced because of mixing of Rydberg s, p, and d orbitals. The calculated excitation energy values are uniformly decreased by about 30%. Large Rydberg s and p orbital participation is found in the excited σ states. Marked diffuse dπ−dπ conjugations are found particularly in the excited ^2B_g state of the DZPD2 calculated result, which leads to the relatively large energy level lowering of the ^2B_g state as compared with the ^2A_u state. Thus, the calculated results indicate that the large Rydberg orbital mixing is generated even in the relatively low-lying excited states of the polysilane oligomer radical anions in the gas phase. There is a possibility that the optical adsorption spectra of polysilane radical anions in the gas phase are different from those in the condensed phase. However, it should be noted that the excited energy level ordering is not so changed between the DZPD and DZPD2 calculated results. The lowest π state energy level ordering, in

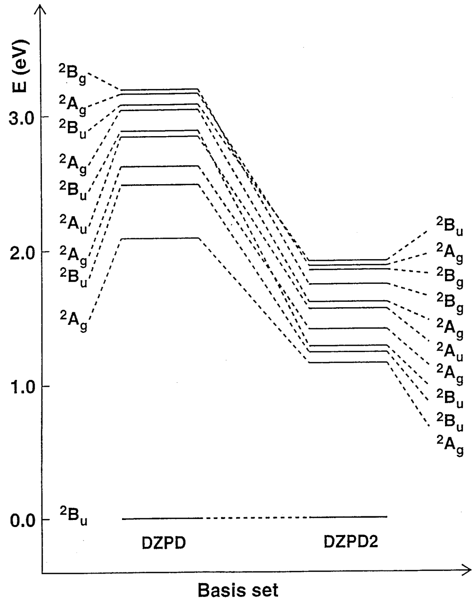

Figure 7. Comparison between the excitation energy levels calculated by the DZPD basis set and those calculated by the DZPD2 basis set in the case of the Si_4H_{10} radical anion.

this case, is rather enhanced from the fourth to the fifth excited state by the mixing of the Rydberg orbitals in this case. This also precludes the possibility that a π-type state becomes a ground state through the participation of diffuse Rydberg $d\pi-d\pi$ conjugations or the Rydberg s and p orbital mixing in the case of polysilane oligomer radical anions.

So the calculated results mainly based on the CIS level of theory clearly precludes the possibility of polysilane oligomer radical anions having a π-type ground state at least in the gas phase. The calculated results also suggest that the π-type ground state is hardly formed in the condensed phase too. This is because it is not expected that the σ-type ground state is easily changed to the π-type one by molecular interactions with surrounding solvent molecules such as MTHF. Considering these results, it is also unlikely that high polymer polysilane radical anions with a π-type ground state are generated in either the condensed or gas phases, at least as far as linear polysilanes are concerned.

Although our calculated results are not consistent with the reported experimental and theoretical results,[13,17] it is a series of methyl substituted oligomer radical anions that were studied in the case of these reported results. Considering this difference in the investigated polysilane oligomer radical anions, there may be a possibility that the methyl substituent might stabilize the π states and changes the electronic state of the ground state from the σ-type state to the π-type one. So we have also carried out an additional and preliminary investigation of the methyl substituent effect on the electronic structure of the polysilane oligomer radical anions by using the 6-31+G(d)[45] basis set. In the case of the Si_2H_6 radical anion, for example, the methyl substituent does not change the ^2B_u σ-type electronic state and destabilizes the SOMO level. The orbital order of the π-type virtual a_u orbital is rather enhanced by the methyl substitution. Our CIS calculation also indicates that the energy level order of the π-type ^2A_u state is enhanced by the methyl substitution. We have not found the tendency that the methyl substitution stabilizes the π-type state of the polysilane oligomer radical anions. There also exists no tendency that the s-type oribital coefficients in the SOMO are decreased by the methyl substitution. From this point of view, it seems unlikely that the electronic structure of the polysilane radical anions is changed from the σ-type state to the π-type one by the methyl substitution.

5. Concluding Remarks

We have theoretically investigated the five polysilane oligomer radical anions including their excited states as model molecules of the polysilane radical anions, putting enphasis on the molecular and electronic structures and their relative stability. The following principal conclusions are derived from the present work.

1. All of the polysilane oligomer radical anions have a σ-type ground state with an unpaired electron occupying a Si−Si σ^* antibonding orbital. The oligomer radical anions with an even number of Si atoms have C_{2h} minimum energy geometries and a ^2B_u electronic state, and those with an odd number have C_{2v} minimum energy geometries and a $^2A_1$ electronic state.

2. Although these polysilane oligomers have negative adiabatic electron affinity values, their oligomer radical anions can exist as bound anions with positive first VIP values.

3. They are stabilized with an increase in the Si−Si main chain length both in terms of the boundness of an unpaired electron and the bonding strength. So it becomes easier to experimentally observe polysilane radical anions according as the chain length is increased, which is consistent with the fact that the smallest polysilane oligomer radical anion experimentally observed so far is the $Si_4(CH_3)_{10}$ radical anion.

4. The π-type states of these oligomer radical anions exist as excited states. The lowest π state level ordering is not lowered but rather enhanced with an increase in the chain length. Although the excited levels can be fairly lowered by the structural change, the π states do not cross the σ ground state for these polysilane oligomer radical anions. According to our calculated results, it is unlikely that radical anions having a π-type ground state are generated in either the condensed or gas phases even in the case of high polymer polysilane radical anions.

5. Although no diffuse Si 3d orbital participation is found in the ground state of the polysilane oligomer radical anions, the $d\pi-d\pi$ conjugations can exist by the mixing of diffuse d orbitals in the excited π states. However, the excited π state energy level ordering is not lowered by the $d\pi-d\pi$ conjugations.

6. Rydberg s, p, and d orbitals fairly lower the calculated vertical excitation energy values of the oligomer radical anions due to Rydberg orbital mixing even in relatively low-lying excited states. However, the Rydberg orbital mixing does not so much affect the excited energy level ordering. There is a possibility that different optical adsorption spectra are observed between polysilane radical anions in the condensed phase and those in the gas phase.

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