(^{1}*JPtC*) = 960 Hz, CPt), 145 (CH=N), 132 (*J*(PtC) = 59 Hz), 131 (*J*(PtC) = 33 Hz), 129 (*J*(PtC) = 48 Hz), 125 (*J*(PtC) = 7 Hz).

[PtClMe$_2$(SMe$_2$){C$_6$H$_4$CH=NPr}] (11c). ^{1}H NMR (acetone-d_6): 0.91 (s, 3 H, ^2J(PtH) = 71 Hz, Me^{a}Pt), 1.16 (s, 3 H, ^2J(PtH) = 68 Hz, Me^{b}Pt), 2.1 (s, 6 H, MeS), 0.93 (t, 3 H, ^3J(HH) = 7 Hz), 2.9 (m, 2 H), 3.95, 4.10 (m, 2 H), 7.2 (m, 4 H).

[PtMe(SMe$_2$){C$_6$H$_3$FCH=NC$_6$H$_5$}] (10b). The compound crystallizes as red crystals; mp 125 °C dec. ^{1}H NMR: δ = 1.04 (s, 3 H, ^2J(PtH) = 84 Hz, Me^{a}Pt), 2.10 (s, 6 H, ^3J(PtH) = 26 Hz, MeS), 8.92 (s, 1 H, ^3J(PtH) = 52 Hz, CH=N), 6.75 (m, 1 H), 7.5 (m, 3 H), 7.3 (m, 4 H). ^{19}F NMR: δ = −116 (dd, *J*(PtF) = 56 Hz, *J*(FH) = 6 Hz, *J*(FH) = 10 Hz).

[PtMe(SMe$_2$){C$_6$H$_4$CH=NC$_6$H$_5$}] (10a). The compound crystallizes as orange crystals; mp 158 °C dec. Anal. Calc for $C_{16}H_{19}NPtS$: C, 42.5; H, 4.23; N, 3.10. Found: C, 42.7; H, 4.36; N, 3.29. ^{1}H NMR: δ = 1.0 (s, 3 H, ^2J(PtH) = 83 Hz, Me^{a}Pt), 2.2 (s, 6 H, ^3J(PtH) = 26 Hz, MeS), 7.65 (d, ^3J(H^{m}H^n) = 8 Hz, 1 H, ^3J(PtH) = 60 Hz, H^m), {7.5 (m, 3 H), 7.3 (m, 4 H), 7.1 (t, 1 H, *J*(HH) = 8 Hz), other aryl protons}.

[PtMe(SMe$_2$){C$_6$H$_3$NO$_2$CH=NC$_6$H$_5$}] (10c). The compound is an orange solid; mp 128 °C dec. Anal. Calc for $C_{16}H_{18}N_2O_2SPt$: C, 38.6; H, 3.6; N, 5.6. Found: C, 38.4; H, 3.4; N, 5.3. ^{1}H NMR: 1.06 (s, 3 H, ^2J(PtH) = 83 Hz, Me^{a}Pt), 2.13 (s, 6 H, ^3J(PtH) = 28 Hz, MeS), 9.40 (s, 1 H, ^3J(PtH) = 56 Hz, CH=N), 8.05 (d, 1 H, ^3J(HH) = 8 Hz, ^{3}(*PtH*) = 60 Hz), 7.7 (d, 1 H, ^3J(HH) = 8 Hz), 7.5 (m, 3 H), 7.3 (m, 3 H).

X-ray Structure Analysis. Crystals of [PtClMe$_2$(ClC$_6$H$_3$CH=NCH$_2$CH$_2$NMe$_2$)] (**7b**) were grown from CH_2Cl_2/pentane. A poor quality yellow block (dimensions 0.42 × 0.34 × 0.61 mm) was chosen and mounted on a glass fiber.

Cell constants and the orientation matrix for data collection were determined by using a CAD4 diffractometer, using 22 reflections in the range $12 < \theta < 15°$. From the systematic absences of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ and from subsequent least-squares refinement, the space group was determined unambiguously to be $P2_12_12_1$ (No. 19). Further details are in Table V.

Data were collected to a maximum of 54° in 2θ. Of 1985 reflections collected, 1898 were unique. Lorentz and polarization corrections were applied. During data collection, the intensities of three standard reflections remained constant (±0.7%), and hence, no decay correction was applied. An empirical absorption correction (DIFABS) was applied.

A total of 1348 reflections with $I > 3\sigma(I)$ were used in the solution and refinement. The structure was solved by using the Patterson method and subsequent difference Fourier syntheses using SDP Plus.[15] In the refinement, hydrogen atoms were included (C–H = 0.95 Å) but restrained to ride on the atom to which they are bonded. The refinement converged to $\Delta/\sigma = 0.02$ with $R = 0.033$. Scattering factors were taken from ref 16; anomalous dispersion effects were included in F_c. The space group is polar, and calculations with each hand led to a slightly lower R factor and better esd's with the model corresponding to the coordinates in Table VI.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Supplementary Material Available: Tables of general temperature factor expressions, calculated hydrogen atom coordinates, torsion angles, and least-squares planes (5 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Electronic Structures of Simplified Polymeric Organosilicon Systems Containing π-Conjugated Moieties

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The electronic structures of several kinds of simplified polymeric organosilicon systems containing a disilanylene (-Si-Si-) or disilenylene (-Si=Si-) unit in the π-conjugated linear organic chain are studied in detail with respect to their optimized geometries on the basis of the one-dimensional tight-binding self-consistent crystal orbital method. The results strongly suggest that in the polymers with the disilanylene unit the electrical conduction mechanism throughout the polymer skeleton should utilize the σ-type crystal orbital as the conduction path and that a special π-type bonding between the Si atom and the attaching substituents could be expected. The fundamental difference between the π-bonding behavior of the silicon-containing polymers and the ordinary organic π-conjugated polymers is also pointed out.

Introduction

Recently, polymeric organosilicon systems have been attracting much attention from both theoretical and experimental points of view,[1] due to their intriguing properties such as semiconducting behavior,[2-4] enhancement of electrical conduction with doping,[5] photoconduction,[6-9]

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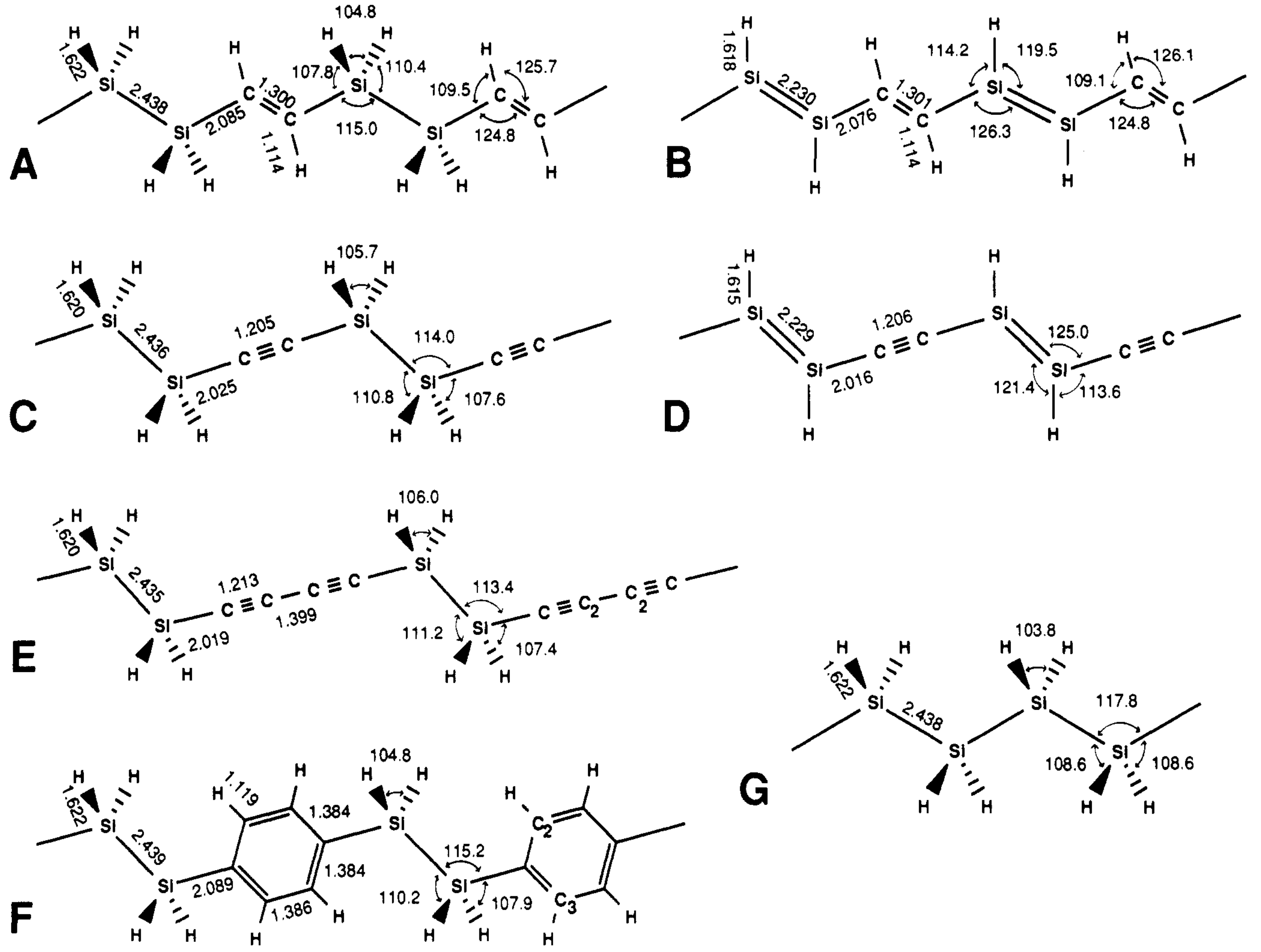

Figure 1. Skeletons of the model polymers (A–F) employed in the present study. The electronic structure of (G) polydihydrosilane (PS) is also checked for comparison. The bond lengths (Å) and angles (deg) indicated are those obtained by the energetical optimization process.

nonlinear optical property[10] and thermochromism.[11,12] It is interesting to note that the fundamental skeletons of most of these polymers consist of a σ-electron network, that is, saturated silicon–silicon bonds. Studies of the electronic structures of polymeric organosilicons such as polysilane derivatives have been well documented.[4,13-20] Furthermore, we have also studied several hypothetical unsaturated silicon and organosilicon polymers as the analogues of polyacetylene and polyacene, where it has been predicted that these polymers have band gap values similar to those of the ordinary π- conjugated organic conductive polymers.[21]

On the other hand, several numbers of interesting polymeric organosilicon systems, which have the combination of regular alternation of a disilanylene unit and carbon π-conjugated moiety such as ethenylene (–C=C–), ethynylene (–C≡C–), diethynylene (–C≡C—C≡C–), butenyne (–C=C—C≡C–), or phenylene group in the backbone, have been synthesized in recent years.[22-26] Most of these polymers are soluble in organic solvent and air stable, showing the electrically conducting properties (σ

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Table I. Electronic Properties of Each Polymer[a]

polymer	A	B	C	D	E	F	PS
effective mass at the top of the HO band[b]	−0.15 (σ)	−0.23 (π)	−0.35 (σ)	−0.22 (π)	−0.21 (σ)	−0.31 (σ)	−0.11 (σ)
effective mass at the bottom of the LU band[b]	0.25 (σ^*)	0.18 (σ^*)	0.94 (σ^*)	0.28 (π^*)	2.60 (σ^*)	1.65 (σ^*)	0.27 (σ^*)
HO bandwidth	2.15	1.26	0.73	1.37	1.66	1.12	5.10
LU bandwidth	0.98	1.40	0.37	0.98	0.06	0.14	1.23
band gap[c]	9.58 (4.10)	8.90 (3.81)	12.64 (5.41)	9.14 (3.91)	12.26 (5.25)	10.90 (4.67)	10.58 (4.53)[i]
exptl value of the band gap[d]	4.77[e]		5.12[f]		5.28[g]	4.88[h]	3.70[i]
ionization pot.	9.58	9.01	12.32	9.18	11.90	10.34	10.59
electron affinity	~0	0.10	−0.32	0.04	−0.36	−0.55	0.01

[a] All the values are shown in electronvolts except the effective mass with the unit of the mass of a free electron (m_0). [b] The type of the band is shown in the parentheses. [c] The values in parentheses are reestimated by a proportional scaling to the value obtained for PS. [d] The values for the actual polymers with different substituents (methyl and phenyl groups) other than hydrogens. [e] From ref 24. [f] From ref 25. [g] From ref 26. [h] From ref 22. [i] From ref 15.

= 0.5-2 S cm^{-1} at room temperature) upon doping with SbF_5.[22-26] This kind of polymer is of much interest as a novel conductive material located at the in-between area of organic and inorganic conductive polymers. In this sense, it will be worthwhile examining their electronic properties based on the theoretical analysis.

In this paper, we study the electronic structure of six kinds of such polymers that contain a disilanylene (–Si—Si–) or disilenylene (–Si═Si–) unit and carbon π-conjugated moieties, as illustrated in Figure 1. The polymers, A, C, E, and F have actually been synthesized with different side substituents such as methyl, ethyl, and phenyl groups. Here we employ hydrogen atoms for these side substituents for simplicity. Although the polymers B and D have not yet been prepared, it would also be of interest to check the electronic structures of these for the sake of comparison.

Method of Calculation

All of the calculations were performed on the basis of the one-dimensional tight-binding self-consistent field–crystal orbital (SCF–CO) method at the level of the CNDO/2 (complete neglect of differential overlap, version 2) approximation including all the valence electrons.[27] The choice of this level of the calculation has come from the comparison of the results of the ab initio (STO-3G basis set) calculations of polymers G and A (see Figure 1). That is, for both G and A, the sequence and nature of the energy bands around the Fermi level, being most important in the present study, had resulted in no significant difference with respect to the present semiempirical and the ab initio[20,28] calculations. It has also been reported[19] that the conformational dependence of the ionization potential and the band gap of G obtained by the ab initio method is consistent with the semiempirical calculations of oligomers of G.[13,14] Polarization functions, such as silicon 3d atomic orbitals (AO's), were suppressed, since it has not been reported that they do not give an appreciable contribution to the electronic structures of silicon atoms in silane oligomers.[17] The number of representative wave vectors was chosen as 21 with regular intervals ($\pi/10a$, where a is the unit vector of the translational symmetry) in the Brillouin zone. The overlap integrals and the electron repulsion integrals were considered as far as the fifth or the seventh nearest-neighboring cell (40–48 Å), depending on the length of the unit cell of each polymer.

The geometries of all the polymers were optimized by using the energy gradient method, the principle of which has been described elsewhere,[29] prior to the examination of the electronic structures. The density of states (DOS) and the π-DOS were evaluated in the conventional manner.[30]

Results and Discussion

Optimized Geometries. Geometrical parameters of all the polymers obtained by the enery gradient method are also shown in Figure 1. The data of polydihydrosilane (PS) calculated by the same method are listed for the sake of comparison. All of the present polymers show C_s symmetry with the planar main-chain skeleton, although we have also checked the manifold in the energy hypersurface to break down the C_s symmetry. It is seen that the Si–C bond length tends to fluctuate due to the condition of the neighboring bonds. The bond angles at Si atoms of B and D are larger than those of A and C, respectively, as a matter of course, due to the change of the hybridization characteristics from sp^3 to sp^2 on the Si atoms.

Electronic Structure. The band structures and the DOS obtained for the polymers are shown in Figure 2. Since all of the present polymers possess C_s symmetry, the CO's can be classified into the σ- and the π-types. These polymers, except C, show a direct band gap in the k (wave vector) space. Both of the highest occupied CO (HOCO) and the lowest unoccupied CO (LUCO) of the models of the actually synthesized polymers (A, C, E, and F) containing the disilanylene unit are of the σ-type. The π-type CO's are observed as the subjacent ones to the HOCO and the superjacent ones to the LUCO. On the other hand, in the polymers B and D having the disilenylene unit, both the HOCO and the LUCO show the π-nature as a whole. Hence the frontier-orbital nature seems to be decided by the existence of either a disilanylene or disilenylene unit.

The patterns of the HOCO and the LUCO of these polymers are illustrated in Figure 3. In the polymers containing the disilanylene unit, i.e., A, C, E, and F, the HOCO is of the pσ bonding state along the polymer skeleton and the LUCO is of the antibonding combination of the 3s AO's of Si atoms, which is similar to those of polysilane already reported.[15-17] The AO's of the carbon atoms of E and F almost do not contribute to the LUCO pattern. Furthermore, the occupied π-type CO subjacent to the HOCO lies in a considerably deeper level (less than −10 eV) compared with the π-type HOCO of B and D. The patterns of these π-type occupied and unoccupied CO's subjacent to the HOCO and superjacent to the LUCO, respectively, of A, for instance, are shown in Figure 4. It is interesting that the pattern of the occupied π-type CO shows the Si–Si antibonding nature and, on the contrary, that of the unoccupied π-type CO the Si–Si bonding nature. This signifies that there is Si–H_2 bonding of pseudo-π-type, as illustrated in Figure 4c and that the energy level of such an occupied CO is even more stable than those of B or D. On the other hand, the π-type CO's making up the HOCO and the LUCO of B and D are more "natural" in their patterns, since in the HOCO the π bonds exist at the –Si═Si– and the –C═C– or –C≡C– units.

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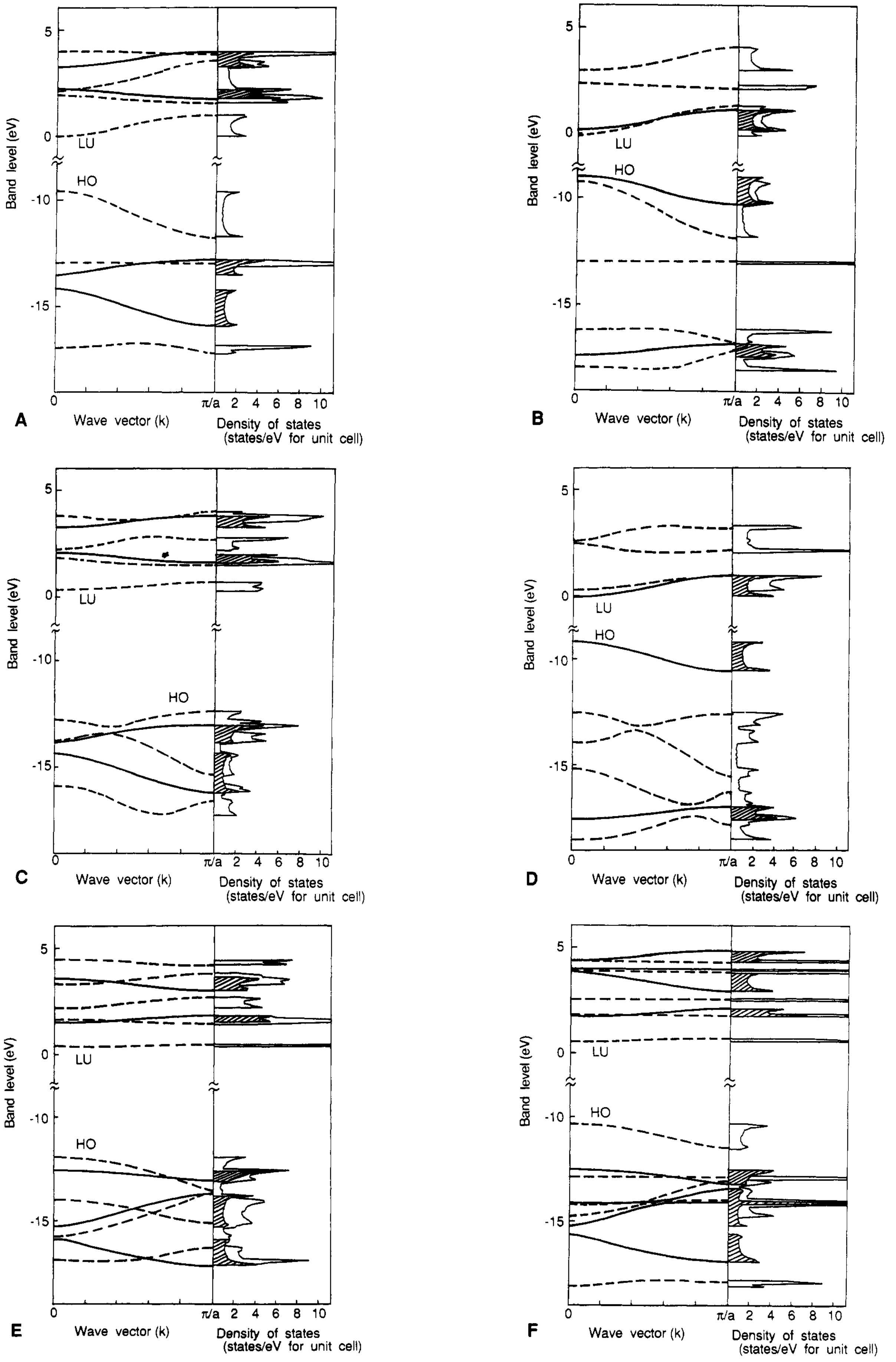

Figure 2. Band structures and densities of states (DOS) of the polymers (A–F) in Figure 1. Broken and solid lines indicate σ and π bands, respectively. The hatched area in the DOS represents the π-DOS.

Table II. Calculated Results of Electronic Structures[a]

polymer		A	B	C	D	E	F	PS
π-bond order	Si—Si	0.138		0.138		0.138	0.138	0.139
	Si=Si		0.972		0.971			
	C=C	0.984	0.973				0.660 0.661 0.669	
	C≡C			0.983	0.973	0.950		
	Si—C	0.126	0.165	0.130	0.165	0.140	0.126	
	Si—H[b]	0.681	0	0.681	0	0.680	0.681	0.682
AO density	Si π	0.814	1.005	0.813	1.007	0.815	0.816	0.830
	σ	2.877	2.854	2.806	2.781	2.788	2.875	2.935
	C π	0.995	0.995	0.995	0.993	1.009	0.994	
	σ	3.066	3.051	3.144	3.127	3.162	3.065	
	C_2 π					0.985	1.002	
	σ					3.005	2.980	
	C_3 π						0.997	
	σ						2.978	
atomic net charge	Si	+0.308	+0.141	0.381	+0.212	+0.397	+0.309	+0.235
	C	−0.061	−0.046	−0.139	−0.120	−0.170	−0.059	
	C_2					+0.010	+0.018	
	C_3						+0.024	
	H(Si)	−0.125	−0.102	−0.121	−0.092	−0.119	−0.126	−0.118
	H(C)	+0.003	+0.007					
	H(C_2)						−0.024	
	H(C_3)						−0.018	

[a] The numberings of carbon atoms of E and F are designated in Figure 1. [b] Between the 3pπ AO of Si and the 1s AO of H.

The electronic properties derived from the band structures are listed in Table I. It is seen that the values of effective mass at the top of the HO band and at the bottom of the LU band do not differ so much between those of the π- and σ-types. Similar tendency is seen with respect to the HO and the LU bandwidths, except for PS. These suggest that there would be no significant disadvantage to the apparent electrical conduction in the polymers consisting of the sp^3-hybridized silicon chain in contrast with that in the sp^3-hybridized carbon chain.

The band gap values are almost the same as or slightly larger than that of PS. These values decrease with changing from the sp^3 silicon to the sp^2 ones in the polymer chain. Nonetheless, its difference is not so large in contrast with the cases of polyethylene and polyacetylene (18.52[31] and 7.46 eV,[32] respectively) or polysilane and polysilacetylene (10.58 and 4.85 eV,[21] respectively), calculated with the same method. It has been pointed out that the Hartree-Fock theory, on which the present SCF–CO method is based, has a tendency toward overestimation of the band gap.[33] The figures in parentheses in Table I are the values obtained by proportional scaling to the value of PS estimated from the experimental data of poly(methylpropylsilane) and poly(methylphenylsilane).[15] These scaled values agree well with those of the absorption spectra of the actual polymers with methyl and phenyl substituents attached to each Si atom.[22-26] Therefore, the observation of a strong absorption in the UV region is assigned to the σ-σ* interband transition described above. The values of the ionization potential (I_p) are slightly larger and those of the electron affinity (E_a) are smaller than those of *trans*-polyacetylene (7.82 and 0.36 eV, respectively[32]). Generally, the value of the electron affinity is less reliable irrespective of the calculation levels, since the Hartree-Fock scheme in the CO method fails to give quantitative data for the physical properties concerning the unoccupied CO's. In this sense, the values of E_a should be interpreted as qualitative ones. These tendencies suggest that the polymeric organosilicon systems require stronger dopants such as SbF_5[5,22-26] to inject the conduction carriers compared with the ordinary organic conductive polymers.

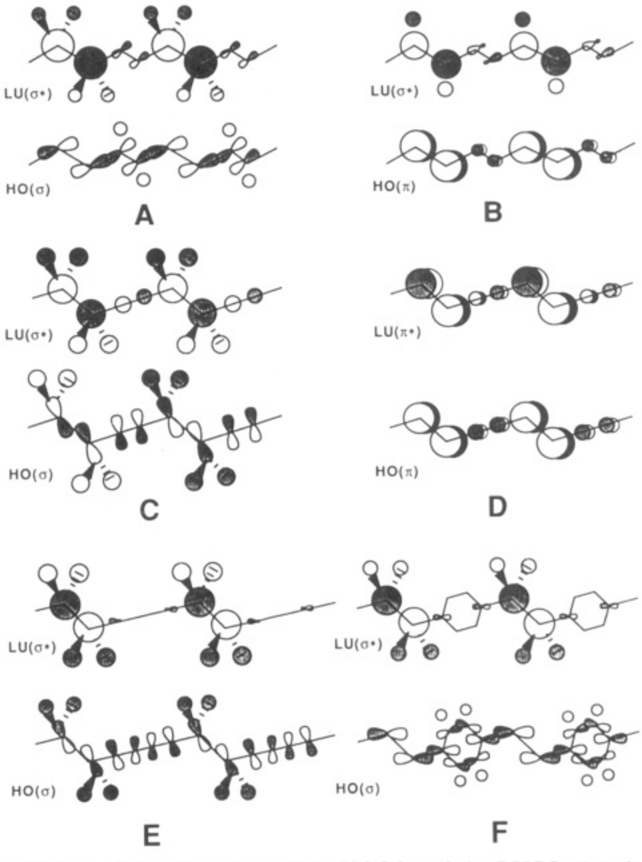

Figure 3. Orbital patterns of the HOCO and the LUCO of each polymer. The polymer skeletons are the same as those shown in Figure 1.

The π-bond orders, AO densities, and atomic net charges are listed in Table II. The degrees of π-bond orders of Si=Si, C=C, and C≡C bonds are almost the same. On the other hand, those of Si—C and Si—Si bonds are very small, which indicates that π-electrons on Si influence little

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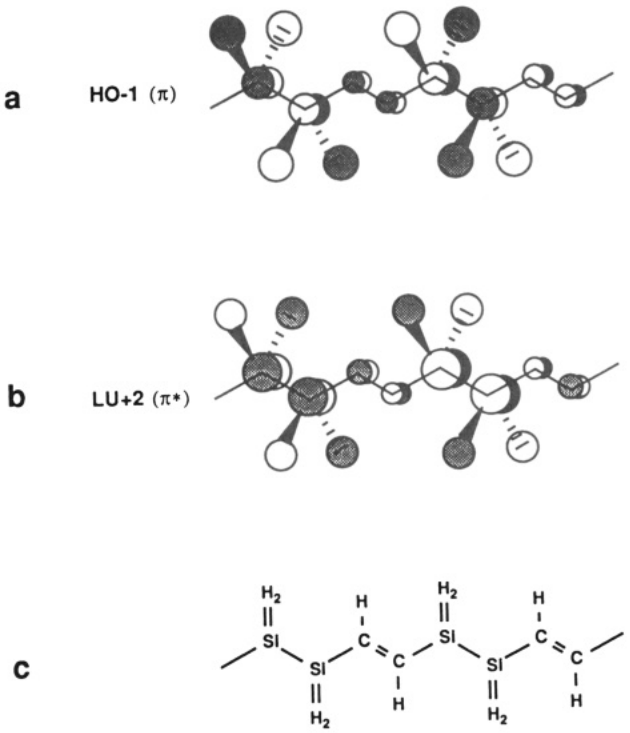

Figure 4. Orbital patterns of the nearest π-type CO's to the HOCO and the LUCO: (a) (HO − 1)CO; (b) (LU + 2)CO. A possible π-bonding mode of polymer A is indicated in (c).

on the Si—C bond. This result explains that the Si—C bond length remains almost unchanged in spite of the change of the electronic condition of Si. Both the hydrogen and carbon atoms attached to silicon atoms are negatively charged in all the polymers, obviously due to the deviation of the σ-electrons. Actual phenyl substitution of hydrogen attached to silicon atoms, particularly in A, C, E, and F, may increase the positive charge on silicon due to the electron-withdrawing property of the phenyl group, resulting in a lowering of the energy level of the unoccupied CO. This may further cause the mixing of the σ and π bands, as has been discussed in the electronic structure of poly(phenylsilane).[15] In any case, such substitution would result in an interesting effect to the electrical conduction mechanism, although it is theoretically yet unclear at the present stage.

Conclusion

We have studied the electronic structures of simplified polymeric organosilicon systems containing a disilanylene or disilenylene unit and carbon π-conjugated moieties such as ethenylene, ethynylene, diethynylene, and phenylene. It has been concluded that the actually synthesized organosilicon polymers containing a disilanylene unit should use the σ-type CO's as the electrical conduction path, since their frontier bands are of σ-type and the bonding π-type CO's, for instance, are much more stabilized. This automatically justifies the interpretation of the σ–σ* interband transition frequently observed in the actual polymeric systems. Furthermore, these polymers tend to form the pseudo-π bonding of the Si–H_2 moiety. Such behavior suggests a possible generation of π-type linkages of Si with the attached substituents, which can be rarely expected in the organic π-conjugated polymers. In turn, it has been made clear that the fictitious polymers containing the disilenylene unit show the ordinary π-conjugated structures throughout the polymer chain, as expected from organic π-conjugated polymers.

All of these tendencies show remarkable differences in electronic properties and, even more, in the solid-state properties of polymeric organosilicon systems. Some of these properties such as electrical conduction mechanism are being examined in our laboratory and will be reported in the near future.

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