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Electronic Structures of Polymers Containing Carbon Multiple Bond and Disilane Units in Their Backbone[†]

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ABSTRACT: The electronic structures of poly(ethynylenedisilanylene) **PED** $(Si_2H_4C_2)_x$ and both *cis*- and *trans*-poly(vinylenedisilanylene) **PVD** $(Si_2H_4C_2H_2)_x$ are studied by means of the ab initio crystal orbital calculations with 6-31G* and 3-21G basis sets. **PED** in its antiperiplanar form shows σ/π conjugation; however, for **PVD**, of the three possible conformers studied only *skew* can be classified as σ/π. In fact, the anticonformer of **PVD**, the one usually found drawn in the literature, displays only σ conjugation and should be unstable, according to vibrational frequency analysis. *Eclipsed* and *skew* structures are minima for **PVD**; the eclipsed conformer displays π conjugation, but the skew conformer is true σ/π and the global minimum for **PVD**. *cis*-Configurational isomers for **PVD** are higher in energy than the *trans*-isomers. Analyses of the ionization potential and the effective hole mass suggest that **PED** is delocalized, but the properties of **PVD** are highly dependent on conformation: anti **PVD** and eclipsed **PVD** are localized, but skew **PVD** is predicted to have a lower ionization potential than **PED**. Overall, the electronic delocalization of **PVD** and **PED** is inferior to that of either pure polysilane or pure polyacetylene, because the nature of σ/π conjugation is not very effective.

1. Introduction

Polysilane high polymers have attracted much attention because of their interesting electronic properties.[1,2] The polymer backbone, which consists of only Si−Si single bonds, is able to support delocalized electron states through its σ bonds. In a previous paper,[3] we examined the electronic structure of the parent polysilane and gave a clear definition of σ conjugation. In addition, we compared the properties of organic π-conjugated polymers (e.g., polyacetylene) with the properties of polysilane. Both π- and σ-conjugated polymers are characterized by small ionization potentials and light holes which can move long distances along the chain. Electron delocalization in π-conjugated polymers occurs in the overlap of the π orbitals perpendicular to the plane containing the atoms of the polymer. On the other hand, electron delocalization in polysilane occurs within the skeletal axis by σ delocalization.[1,2]

Recently, many workers have succeeded in the synthesis of alkyl- and aryl-substituted poly(ethynylenedisilanylenes),[4] analogues of the parent compound, **PED**, $(Si_2\ H_4\ C_2)_x$, and poly(vinylenedisilanylenes),[5] analogues of the parent compound, **PVD**, $(Si_2\ R_4\ C_2\ H_2)_x$. These polymers, which contain both carbon multiple bonds and Si−Si bonds in their backbone, absorb light in the UV range of the spectrum and display high conductivity when doped.[4,5] Because the mechanism for electronic delocalization is based on σ/π mixed conjugation, these systems can be classified as a third type of conjugation involving both π conjugation (e.g., polyacetylene) and the σ conjugation of polysilane.

Tanaka et al.[6] and others[7] reported electronic structure calculations on various σ/π-mixed polymers using the semiempirical CNDO/2 approximation. We deemed such an approximate approach to be insufficient to meaningfully assess the efficiency of σ/π conjugation compared with either σ or π conjugation by itself.[8] Furthermore, the authors did not take into account the effects of σ/π orbital overlap, which creates a multifaceted potential energy surface for **PVD**. In fact, the anti form of **PVD**, which is the only conformer of this polymer considered in the previous work, turns out to be a transition state, relaxing to either the *skew* or *eclipsed* forms.[9] Moreover, as we will show later, the anti conformer of **PVD** is formally not σ/π-conjugated at all, because the orbitals are orthogonal to each other.

In this article, we report the more reliable results of both ab initio molecular orbital calculations of the monomers and the ab initio crystal orbital calculation of the parent polymers, **PVD** and **PED**.[10] Although our method cannot produce reliable values for the band gaps of the polymers studied here, the ground-state geometries and relative energies of the polymers should be adequate for an descriptive understanding of σ/π conjugation. Note that the analysis of the energy band structures will become a very useful tool for the study the optical properties of the polymers, such as ultraviolet photoelectron/X-ray photoelectron spectra.

2. Method of Calculation

Ab initio molecular orbital calculations are performed on the model monomers ethynyldisilane and vinyldisilane with 3-21G[11,12] and 6-31G* basis sets[13,14] using the Gaussian 94 program package.[15] We also performed the MP2/6-31G* optimizations on these molecules. The electronic structures of **PED** and **PVD** are calculated with full geometry optimization by the ab initio crystal orbital method[16,17] with 6-31G*[13] and 3-21G basis set.[11,12]

The Namur-type cutoff method is applied on the integral cutoff up to the fifth-neighbor (3-21G) and tenth-neighbor (6-31G*) without the multipole expansion technique.[19,20] About half of Brillouin zone, 21 K points, are taken for the numerical integration of the density matrix elements.[20] The energy gradient method for one-dimensional polymers proposed by Teramae et al.[22,23] is used for the optimizations of the polymer

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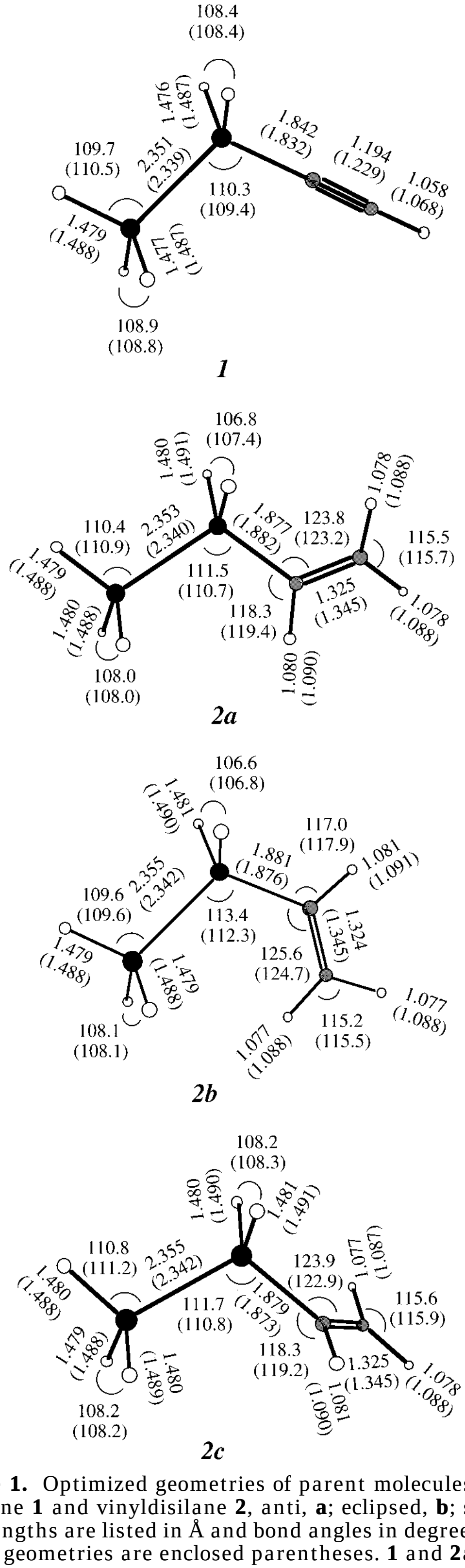
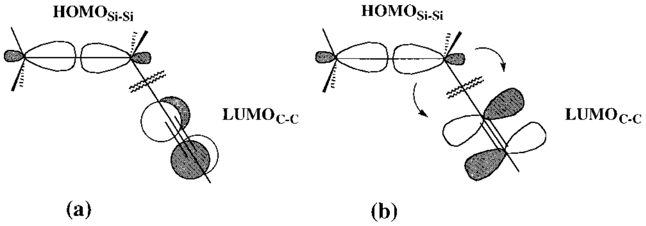


Figure 1. Optimized geometries of parent molecules ethynyldisilane **1** and vinyldisilane **2**, anti, **a**; eclipsed, **b**; skew, **c**. Bond lengths are listed in Å and bond angles in degrees. MP2/6-31G* geometries are enclosed parentheses. **1** and **2a**−**b** are C_s point groups; **2c** is C_1 symmetry. The dihedral angle for Si−Si−C−C is 116.4 (115.6).

structures. The vibrational frequencies of polymers are calculated by the numerical differentiation of the first derivatives obtained by the energy gradient method. Note that the vibrational degree of freedom of 1-D polymers is 3N-4, where N is the number of atoms in the unit cell, because rotation perpendicular to the polymer axis is impossible. The effective masses of hole, m_h*, and electron, m_e*, are calculated by the least-squares fit of the energy band.[3,24]

Scheme 1. Orbital Mixing Scheme of σ_{Si-Si} (HOMO) and Degenerate π^*_{C-C} (LUMO) for 1. (a) The π Orbitals Are Out-of-Plane, Orthogonal to the σ_{Si-Si}; (b) The π Orbitals Are In-Plane, Providing Good Overlap for the σ_{Si-Si}



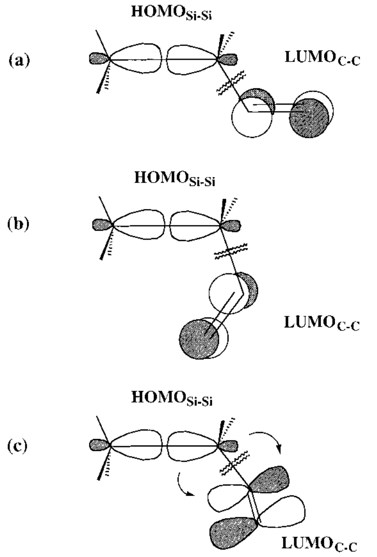
3. Results and Discussion

Monomers. The HF/6-31G* and MP2/6-31G* optimized geometries of the model compounds, ethynyldisilane **1** and vinyldisilane **2a**−**c**, are shown in Figure 1. At HF/6-31G* the optimized C−C bond distances, 1.194 Å for **1** and 1.324−5 Å for **2**, are noticeably longer than the C−C bond in acetylene (1.180 Å) and ethylene (1.317 Å). The observed bond lengthening results from increased population of π^*_{C-C} by the charge-transfer interaction from the σ_{Si-Si}. Frontier molecular orbital analysis permits us to make a simplified model of the charge transfer from the highest occupied molecular orbital (HOMO) of the disilane unit to the lowest unoccupied molecular orbital (LUMO) of the alkene or alkyne, as shown in Schemes 1−3. As we shall see, ethynyldisilane can make efficient overlap of the σ_{Si-Si} -π^*_{C-C} orbitals, maintaining C_s symmetry, but vinyldisilane must undergo an asymmetric distortion to maximize the overlap between the two orbitals. Scheme 1 shows a simplified picture of the charge-transfer interaction of the HOMO$_{Si-Si}$ of a disilanyl unit with the LUMO$_{C-C}$ of an ethynyl unit. Although there is no overlap in the out-of-plane π^* orbitals, the degenerate in-plane π^* orbitals provide good overlap. **1** has inherent σ/π overlap within C$_s$ symmetry.[25]

On the other hand, the anti structure **2a**, the closest analogue of **1**, in which the vinyl group extends antiperiplanar to the Si−Si bond, is not a minimum structure. The vibrational frequency analysis of **2a** gives one imaginary frequency (92.3i cm^{-1} with the 3-21G basis set), and the structure is predicted to be a transition state. For **2a** there is only one set of $\pi^*_{C=C}$ orbitals, and this pair is orthogonal to the σ_{Si-Si} orbitals (Scheme 2a). The other C$_s$ structure **2b** in which the vinyl ligand *eclipses* the Si−Si bond is also deprived of effective overlap by the orthogonal relationship of the HOMO$_{Si-Si}$ and LUMO$_{C=C}$ orbitals (Scheme 2b). However, **2b** is stabilized more than **2a** by the secondary interaction of the HOMO-1$_{Si-Si}$ (π-type) orbitals with the $\pi^*_{C=C}$ orbitals as seen in Scheme 3, a and b. This interaction is more effective between the orbitals on the terminal Si and terminal C in the eclipsed structure (Scheme 3b) than in the anti structure (Scheme 3a). In fact, **2b** is minimum on the potential energy surface but not the global minimum.

The global minimum, **2c**, is *skewed* such that the vinyl group is almost eclipsing one of geminal Si−H bonds. **2c** can be obtained by decreasing the symmetry of **2a** to C_1 according to the normal coordinates of the imaginary frequency of **2a**. The skew structure is the most stable conformer because the overlap between the $\pi^*_{C=C}$ and the σ_{Si-Si} and σ_{Si-H} is maximized by the folding back of the vinyl ligand as seen in Scheme 2c.

Scheme 2. Orbital Mixing Scheme of σ_{Si-Si} (HOMO) and the π^*_{C-C} (LUMO) for 2. (a,b) 2a−b Are Shown in Their Nonconjugated Configuration. (c) 2c Is Shown in Its Conjugated Configuration



Scheme 3. Orbital Mixing Scheme of π_{Si-Si} (HOMO-1) and π_{C-C} (LUMO). (a) 2a Only Has Overlap between the Orbitals of the Centrally Bonded Si and C, but No Interaction by the Orbitals of the Terminal Atoms. (b) 2b Can Have Overlap between the Orbitals of Both the Central and Terminal Pairs of Si and C Atoms

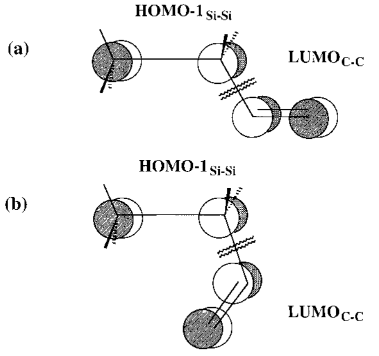


Figure 2 shows the potential energy surface for **2**. The relative energies at HF/6-31G* among **2a**−**c** are shown along with a fourth point, the gauche conformer.[25] Gauche is the transition state structure, between **2b** and **2c**, creating a small barrier of only about 0.8 kcal mol^{-1}. The basic topology of this surface resembles the one calculated and found experimentally for 1-butene.[27] The transition states and the minima are at the same points for 1-butene and vinyldisilane. However, the highest energy barrier is gauche for 1-butene; but for **2**, anti is the highest energy barrier, because for **2**, gauche has better orbital overlap than anti.[28] In addition, the size of the barriers is decreased for **2**. Although the relative energy difference between the skew point and the anti-state is about the same when calculated for **2**, 1.9 kcal mol^{-1} or 1-butene, 2.2 kcal mol^{-1}, but the gauche conformation is more than twice higher for 1-butene than **2**, 2.7 vs 1.2 kcal mol^{-1}.

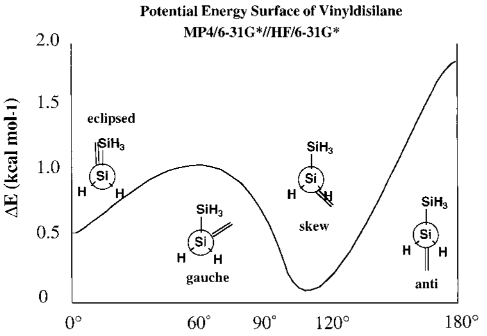


Figure 2. Potential energy surface for vinyldisilane. Relative energies are from fully optimized structures at HF/6-31G*. Single point MP4 results show almost no change. See ref 26.

Table 1. Total Energies of PED and PVD with 3-21G and 6-31G* Basis Sets[a]

polymer	configuration	conformation	3-21G	6-31G*
PED	–	–	−652.400040	−655.866525
PVD	*trans*	anti	−653.566685	−657.039364
		eclipsed	−653.571319	−657.042988
		skew	−653.571615	−657.045138
	cis	anti	−653.557186	−657.028706
		skew	−653.566199	−657.039189

[a] Units are shown in a.u.

Polymers. We performed crystal orbital calculation for the polymers built from the model monomers **1** and **2a**−**c** as unit cells. Although the previous study[6] assumed only the *trans*-configurational isomer of **PVD** polymer, we examined the relative energetics of the *cis*-configurational isomer as well. For *trans*, we considered the major stationary points of the **2a**−**c**, eclipsed, skewed, and anti. For *cis*, since the eclipsed isomer would be unlikely because the 1,6-silylene groups would be forced almost on top of each other, we considered only the skew and anti conformers.

Figure 3 shows the schematic view of the unit cell structures of the polymers, along with the optimized geometrical parameters obtained from the 6-31G* and 3-21G basis sets. The geometries closely resemble optimized HF/6-31G* structures for **1**−**2** from Figure 1. For convenience, we refer to the polymers in terms of point group symmetries[29] within the unit cells. The unit cells for **PED** and **PVD**, *cis*-, *trans*-anti, and *trans*-eclipsed, have C_s local symmetry. Skew **PVD** is based on local C_i symmetry for *trans* and local C_2 symmetry for *cis*.

Table 1 shows the total energies of the polymers. The same order of relative energies seen for the potential energy surface of the monomers **2a**−**c** is preserved for **PVD** by both 6-31G* and 3-21G basis sets. The most stable conformers for both *trans* and *cis* is skew; the least stable is anti. *cis*-Skew, the lowest energy conformer of *cis*- **PVD**, is still higher in energy than *trans*-anti, although the difference is less than 1 kcal mol^{-1}. Therefore, it appears that *trans*-**PVD** is more likely for the linear polymer.

The vibrational frequencies of the five structures of **PVD** are calculated at the 3-21G level, and the results are shown in Table 2. The anti structure for both *trans*- and *cis*-linked polymers **PVD** have one imaginary frequency, making them transition states. The corresponding normal mode for both anti conformers is out-of-plane bending (plane formed by Si−C═C−Si), indicating that this form will not be stable and will relax to skew. We should point out that this is the first time that a transition state of an infinite 1-D system has been located. The other three structures are confirmed to be minima on the potential energy surface.

Table 3 shows the Koopman's ionization potential, (IP), vertical electron affinity, effective mass of hole, and effective mass of electron of polymers. For comparison,

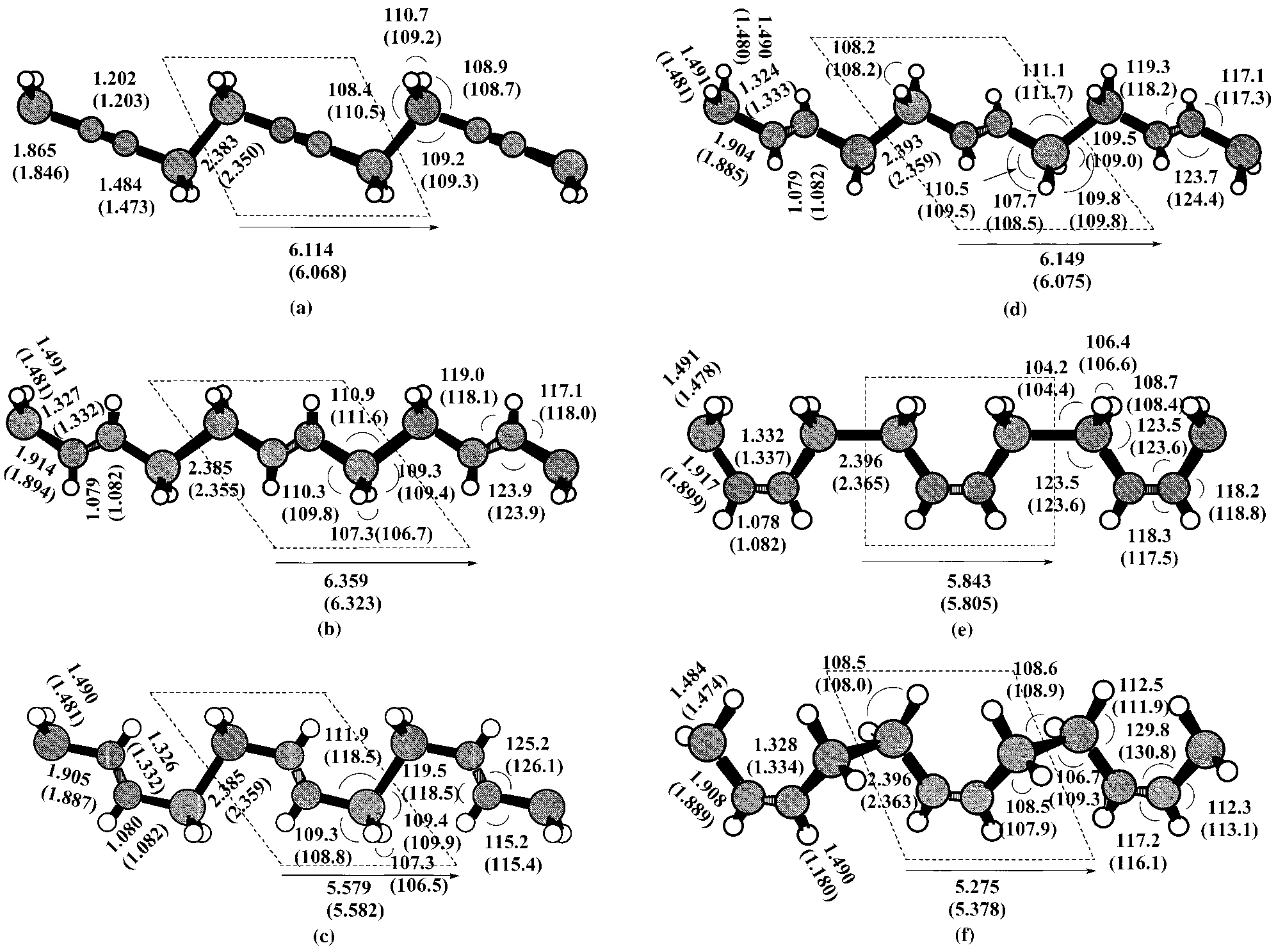


Figure 3. HF/3-21G and HF/6-31G* optimized geometries of parent polymers. (a) **PED**; (b) *trans*-anti **PVD**; (c) *trans*-eclipsed **PVD**; (d) *trans*-skew **PVD**; (e) *cis*-anti **PVD**; (f) *cis*-skew **PVD**.

Table 2. Vibrational Frequencies of PVD

structure		frequencies (cm^{-1})									
trans	anti	117i	168	248	257	367	462	524	715	747	762
		765	805	905	928	1021	1022	1167	1366	1481	1749
		2246	2255	2258	2264	3272	3283				
	syn	112	167	264	390	405	419	510	732	734	742
		762	764	946	961	1029	1030	1167	1356	1479	1760
		2246	2257	2257	2267	3275	3284				
	skew	148	188	235	302	393	421	519	738	738	754
		773	839	883	962	1002	1004	1169	1351	1467	1750
		2254	2255	2265	2265	3277	3287				
cis	anti	98i	190	300	419	430	476	595	687	702	757
		812	823	857	875	997	1033	1190	1312	1491	1711
		2236	2244	2261	2272	3272	3301				
	skew	188	199	330	344	406	513	567	615	672	741
		775	813	862	874	999	1025	1194	1335	1507	1753
		2262	2262	2276	2310	3234	3265				

the values of effective mass of hole and the Koopman's ionization potential of *trans*-polyacetylene and *trans*-polysilane are calculated with the 3-21G basis set at the previously reported 4-31G (polyacetylene) and DZ (polysilane) optimized structures.[3,30] Overall, m_h* and the value of the ionization potential of **PED** and **PVD** are larger than those of *trans*-polyacetylene and *trans*-polysilane. Thus, the semiconducting properties and the hole conductivity of the σ/π systems should not be as effective as the pure π conjugation of *trans*-polyacetylene or the pure σ conjugation *trans*-polysilane. Still, it is worthwhile to compare the properties of the conformers of σ/π-conjugated polymers to understand their behaviors.

The skew form of **PVD** has the lowest IP and smallest band gap among the σ/π polymers, **PED** has the next lowest IP, Because the experimentally observed UV absorption is at lower energy for **PVD** analogues than for **PED** derivitives.

Another important property for evaluating the electronic delocalization along the polymer chain is the effective mass of the hole.

The m_h* of **PED** is relatively small, only three times that of polyacetylene and polysilane. Along with other properties, m_h* of **PVD** strongly depends on the conformation. Because m_h* <1.0 indicates electronic delocalization, all forms of **PVD** except for eclipsed are predicted to be possible hole conductors.

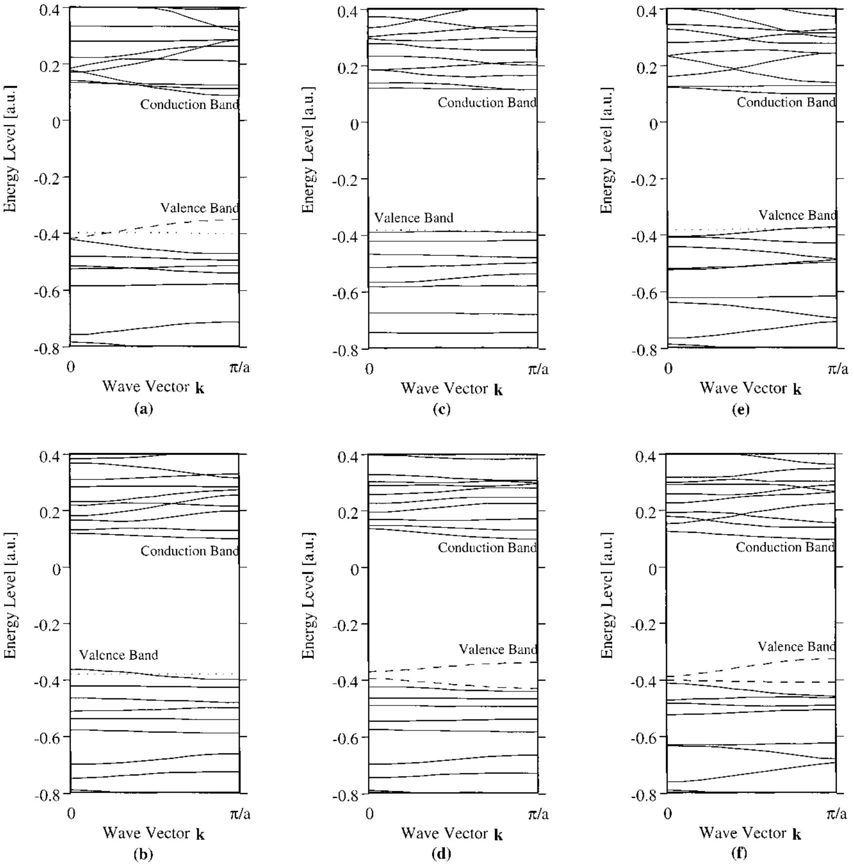


Figure 4. Energy band structures of polymers. (a) **PED**; (b) *trans*-anti **PVD**; (c) *trans*-eclipsed **PVD**; (d) *trans*-skew **PVD**; (e) *cis*-anti **PVD**; (f) *cis*-skew **PVD**. For the highest and next highest valence bands,—indicates pure σ bands; ··· indicates pure π bands; and — — — indicates σ/π.

Table 3. Koopman's Ionization Potential (IP), Vertical Electron Affinity (EA), Effective Mass of Hole (m_h*), and Effective Mass of Electron (m_e*) for Polymers[a]

polymer	configuration	conformation	IP	EA	m_h*	m_e*
PED	–	–	9.61	2.34	0.36	0.30
PVD	*trans*	anti	9.96	2.69	0.35	1.21
		eclipsed	10.42	3.05	3.20	0.38
		skew	9.13	2.53	0.62	0.54
	cis	anti	10.18	2.61	0.46	1.38
		skew	8.97	2.59	0.45	0.87
polyacetylene	*trans*	–	6.50	1.04	0.13	0.24
polysilane	–	*trans*	8.91	1.45	0.17	0.11

[a] Units are shown in eV and mass of free electron.

The small hole mass of anti- **PVD** arises from the effective σ conjugation in the plane of the polymer. *trans*-Polysilane and polyethylene also have small m_h* from the same pathway. Skew **PVD**, which has the most effective σ/π overlap, is about one and a half times **PED**, similar to polysilanes of mixed conformation, which contain one gauche turn in the unit cell. The delocalization pathway seems to be only slightly worsened by the deviation from planarity in these systems, but certainly not obstructed.[31]

Figure 4 shows the energy band structures of **PED** and **PVD** at 3-21G levels.

For eclipsed- **PVD**s the valence band becomes out-of-plane π and the electron density is localized in the π_{C-C} bond (Figure 4c). This out-of-plane π band exists for **PED** (Scheme 1a) and **PVD** (Scheme 2a,b) forms, which are symmetric with respect to a symmetry plane running through the polymer. For these polymers, the two highest VBs are the same (Figure 4a–c,e), one is an in-plane, delocalized σ-type and one is localized mostly on the π_{C-C} orbitals normal to the plane of the polymer. The former creates a dispersed band, the latter a rather flat band. For the polymers with light holes, the disperse σ-type band crosses the flat band, making the VB mixed σ^{32} in-plane. However, for the *trans*-eclipsed conformer because of the orbital mixing, previously discussed in Scheme 3b, the σ band lies under the flat, localized π_{C-C} band (Figure 4c). The hole effective mass of the localized VB is naturally quite high.

For the skew structures, breaking of a symmetry plane, brought on by effective σ/π mixing gives rise to two top valence bands, which are both quite dispersed. No crossing is observed for these bands because the they are not made of separated σ and π, but are mixed σ/π. Because the VB has a great deal of curvature, and starts out at a fairly low IP, the skew- **PVD** conformers have the lowest IP potential. Still, because the polymer backbone does not lie completely extended in a plane, the m_h* is not the lower than **PED**.

Finally, the values of electron affinity, for the σ/π-mixed polymers are rather large positive numbers indicating that these polymers would be poor electron acceptors such as polysilane.[3] The most likely cause for the high electron affinities of the polymers is the contribution to the CB by σ* orbital of the disilanyl moieties. Because the antibonding orbitals affect framework bonds, population of these orbitals is bound to destabilize the polymer.

4. Conclusion

In this article, we have studied the electronic structure of **PED** and **PVD** by means of the ab initio crystal orbital method. Careful analysis of the ionization potential and the effective mass of hole suggest that the electronic conductivity cannot exceed those of polysilane and polyacetylene. However, the phenomenon of σ/π conjugation leads to many possible conformational states within the unit cell of the polymer. Although the anti structure of **PED** is a minimum structure, that of **PVD** is a transition-state structure. This is confirmed by the vibration frequency analysis. Both eclipsed and skewed structures are minima of **PVD**. The skew structure is found to be the global minimum. Furthermore, the *trans*-configuration is more stable than the *cis*. It is likely with large side groups that the *trans*-forms become further stabilized.

The conformational properties of **PVD** are somewhat similar to polysilane, in which side chains determine whether polysilane will be more *trans*-planar or gauche-helical, points both well established as minima on the potential energy surface for polysilane. Two stable states of *trans*-**PVD**, skew and eclipsed, are minima. Skew has small IP and light hole; eclipsed has a higher IP and heavy hole. Consequently, if **PVD** can be manipulated into the extended, skew, from contracted, eclipsed, or vice versa, the polymer may show thermochromic[33] or barochromic[34] behavior like polysilane. As far as we know, there are no reports yet of such behavior for **PVD** analogues.

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(9) Preliminary molecular orbital studies on phenyldisilane show that the antiperiplanar C_s structure, like vinyldisilane, is not a minimum. Therefore, earlier studies regarding mixed σ/π polymers with organic rings in the backbone, poly(phenylenedisilanylene)[6] and poly(thiophenylenedisilanylene)[7] assumed an unstable conformation. Of course, because the phenyl polymer is substituted 1,4 across the ring, the length of the unit cell of poly(phenylenedisilanylene) would not change. However, the band calculation for a skewed phenyl ring may be different from the earlier study because the overlap is decidedly different.

(10) We did not consider the effect of disilenyl units in the polymer backbone like Tanaka et al. because no such polymers are known. Moreover, from our experience with the difficulty of describing the disilene molecule correctly by MO theory, it is not clear how the σ/π overlap would affect the structures of the polymers. See, for example, Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140.

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(25) There is a small rotation barrier of the silicon−silicon bond, but we did not consider it because this rotation should not have any significant effect on the σ/π overlap.

(26) Of course the absolute energies of the four isomers change when electron correlation is included in the calculation, but the relative energies remain almost exactly the same up at MP4/6-31G*//HF/6-31G*: Skew = 0.0; eclipsed = 0.4; gauche = 1.0; anti = 1.8 (units in kcal mol^{-1}).

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(32) **PED** has an actual p-π bonding in the plane of the σ bond (Scheme 1b) making the VB formally σ/π. However, *cis*- and *trans*-anti-**PVD** has only p-σ bonds in the plane of the polymer and no true in-plane π orbitals. Thus, the VB for anti-**PVD** is classified only as σ. Both VBs have the same symmetry and cross the out-of-plane π band. The more effective σ/π overlap of **PED** is seen in its lower ionization potential than **PVD**.

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