Organometallics 1992, *11*, 3178–3184

Articles

Geometrical and Electronic Structures of π-Conjugated Silicon Ring Polymers

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Received February 10, 1992

Two alternative structures of the $[C_4H_2SiR_2]_n$ polymer have been considered. Full geometry optimization at different levels of theory indicate that the five-membered-ring structure (1) is more stable, by about 15 kcal/mol, than the structure with a four-membered ring (2). On the other hand, the electronic structure of polymer 1 indicates a rather low band gap of 1.44 eV, in contrast to the experimental value of 2 eV, while 2 has a calculated band gap of 1.99 eV. Therefore, this structure is more consistent with the experimental absorption spectrum of the polymer than structure 1. This conclusion is also consistent with the NMR data of Wei et al.[2]

I. Introduction

Recently, a novel class of π-conjugated polymetalloles incorporating Si, $[C_4H_2SiR_2]_n$, has been synthesized by polymerization of $R_2Si(C{\equiv}CH)_2$ monomers (R = Me, Bu, Ph).[1] In 1989, a structural model based on spectroscopic analysis was suggested by Shinar et al. arguing that $[C_4H_2SiR_2]_n$ is polysilole 1, a polyheterocycle consisting of five-membered rings (Figure 1). One year later, Wong et al.[2] reported that the $[C_4H_2SiR_2]_n$ polymer should be described as having a four-membered-backbone ring structure, poly(diethynylsilane) 2, as depicted in Figure 1. This structural model is supported by ^{13}C and ^{29}Si nuclear magnetic resonance and resonance Raman scattering measurements[3] and by some ab initio Hartree–Fock calculations of the backbone structure.[4] Both of these proposed structures are in disagreement with the linear $[SiPh_2{-}C{\equiv}C{-}C{\equiv}C{-}]_n$ polymer, proposed by Luneva et al.[5] in 1968.

Silole compounds have been investigated extensively[6-8] (see Figure 2), while four-membered rings containing Si with a carbon exo bond have been synthesized recently[9,10] and four-membered silacyclobutenes are also known.[11] The high strain energy within the ring system may impart to these (*exo*-alkylidene)silacyclobutenes a limited stability, which have to be protected by bulky substitutents, such as $SiMe_3$ or phenyl groups (see Figure 3). Because of this fact, we performed theoretical calculations to predict the relative stability and electronic properties of polysilole and poly(diethynylsilane).

The onset of absorption of conjugated polymers is closely related to the energy gap, E_g, which is very sensitive to the structure of the polymer.[12] The first optical absorption maximum is at 2 eV[1,2] for $[C_4H_2SiR_2]_n$, to be compared with the 1.8-eV value corresponding to *all-trans*-polyacetylene.[13] A successful theoretical calculation should interpret E_g, considering that silicon does not seem to be strongly participating in the delocalized π-electron system.

II. Methodology

We employed a modified neglect of diatomic overlap (MNDO)[14] molecular orbital and energy band method,[12b,c,15] using a recently published parametrization dubbed PM3,[16] with the purpose of determining the heats of formation and thereby the fully optimized

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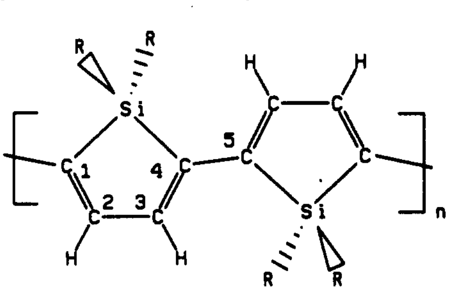

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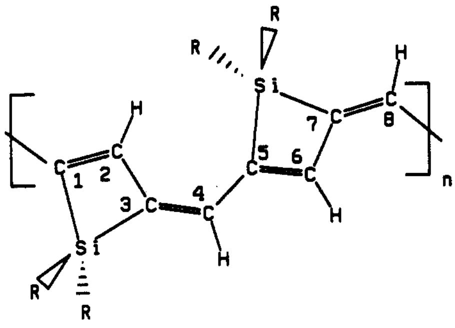

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Figure 1. Two alternative structures of the $[C_4H_2SiR_2]_n$ polymer: (**1**) polysilole; (**2**) poly(diethynylsilane).

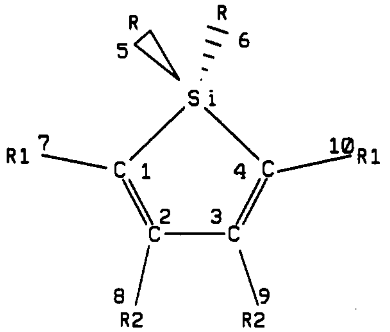

Figure 2. Silacyclopentadiene **3**: (**3a**) R1 = R1 = Ph, R = Me; (**3b**) R1 = Ph; R2 = H, R = Me; (**3c**) R1 = R2 = H, R = Me; (**3d**) R1 = R2 = R = H.

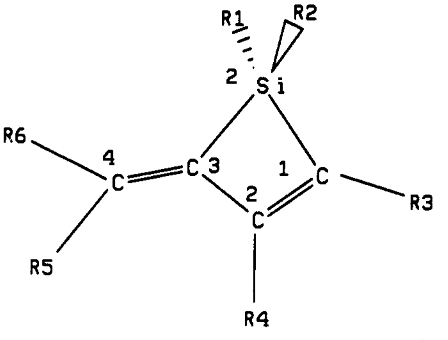

Figure 3. Diethynylsilane **4**: (**4a**) R1 = R2 = R3 = R5 = $SiMe_3$, R4 = R6 = Ph; (**4b**) R1 = R2 = Ph, R3 = CMe_3, R4 = Pt-$(PEt_3)_2(H_2O)^+$, R5 = H, R6 = CMe_3; (**4c**) R1 = R2 = Me, R3 = R4 = R5 = R6 = H; (**4d**) R1 = R2 = R3 = R4 = R5 = R6 = H.

geometries of molecules, oligomers, and polymers related to 1 and 2. The planarity of the polymer backbone has been assumed. It is well-known that solid-state theoretical calculations that are based on the Hatree–Fock self-consistent-field theory grossly overestimate the energy gap of insulators and semiconductors.[17]

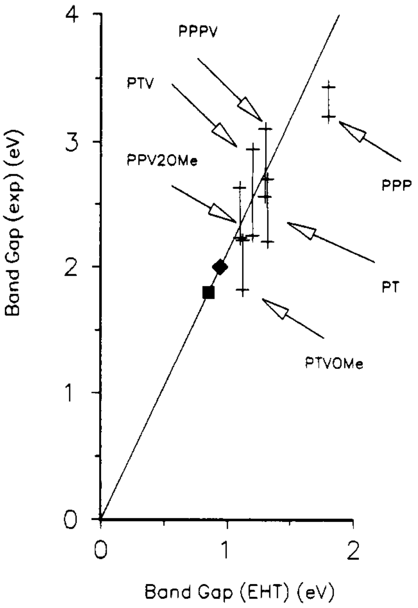

Figure 4. Correlation of EHT values[21] and experimental values[22] for poly(*p*-phenylene) (PPP), poly(*p*-phenylene vinylene) (PPPV), poly(dimethoxy-*p*-phenylene vinylene) (PPV2OMe), polythiophene (PT), poly(thiophene vinylene) (PTV), and poly(3-methoxythiophene vinylene) (PTVOMe): (◆) poly(diethynylsilane); (■) *all-trans*-polyacetylene. Equation 1, $E_g^{\text{scaled}} = 2.12E_g^{\text{EHT}}$, is represented by a thin line.

As a compromise, we have used the extended Hückel theory (EHT)[18,19] to determine E_g and the band structures, using the geometries that we obtained from the fully optimized MNDO PM3 solid-state total energy calculations (parameters for EHT are listed in ref 18c). In our MNDO PM3 calculations, we used a set of 6 *K*-points in the Brillouin zone (52 *K*-points in the EHT band calculations). In order to compare the calculated E_g values and to render them more physically realistic, we introduce a scaling factor, *k*:

$$E_g^{\text{scaled}} = kE_g^{\text{EHT}} \tag{1}$$

We have chosen *k* to fit E_g^{exp} of *all-trans*-polyacetylene (1.8 eV):[13]

$$k = E_g^{\text{exptl}}/E_g^{\text{EHT,PM3}} = 2.12 \tag{2}$$

where the EHT,PM3 index indicates that the gap is calculated by the EHT method using a PM3-optimized geometry.

We define the experimental gap E_g^{exptl} as the peak position, corresponding to the π–π^* transition of the optical spectrum. This is in concordance with the interpretation of Heeger et al.[20] of the one-dimensional band gap of conducting polymers. Another popular choice for E_g^{exptl} is that of the onset of the optical absorption, which corresponds to the three-dimensional band gap. Using the latter would lead to a smaller *k* value but would not change the correlation of the theoretical and experimental E_g values significantly. Figure 4 shows that EHT band structure calculations reproduce the experimentally found variations of the energy gap quite well for a variety of conducting polymers.[12,21] The scaling function $E_g^{\text{scaled}} = kE_g^{\text{EHT}}$ is also shown, and the corresponding band gaps E_g^{scaled} are in agreement with experience. The ranges shown for the experimental data correspond to different experiments.[22]

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Table I. Experimental and Calculated MNDO PM3 Geometry[a] of Silacyclopentadiene Compounds[b]

	3a		3b		3c[c]	3d[c]
	exptl[d]	MNDO PM3	exptl[e]	MNDO PM3	MNDO PM3	MNDO PM3
Si–C(1)	1.868	1.868	1.878	1.872	1.856	1.834
C(1)–C(2)	1.358	1.345	1.345	1.342	1.336	1.339
C(2)–C(3)	1.511	1.483	1.466	1.466	1.471	1.469
Si–R	1.855	1.866		1.889	1.877	1.494
C(1)–C(7)	1.477	1.454		1.453		
C(2)–C(8)	1.487	1.472				
C(1)–Si–C(4)	92.7	91.5		91.2	92.0	93.0
Si–C(1)–C(2)	107.6	107.6		106.8	107.3	107.1
C(1)–C(2)–C(3)	116.0	116.5		117.1	116.6	113.4
$\tau_{1,7}$	117.1	90.8	0–14	76.5		
$\tau_{2,8}$	118.6	89.9				
$\tau_{3,9}$	118.6	89.9				
$\tau_{4,10}$	117.1	90.8	0–14	76.5		

[a] Bond lengths are in angstroms and bond and dihedral (τ) angles in degrees. Atom numbering is depicted in Figure 2. [b] **3a**, 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene (R = Me; R1 = R2 = Ph); **3b**, 1,1-dimethyl-2,5-diphenylsilacyclopentadiene (R = Me; R1 = Ph; R2 = H); **3c**, 1,1-dimethylsilacyclopentadiene (R = Me; R1 = R2 = H); **3d**, silacyclopentadiene (R = R1 = R2 = H). [c] No experimental geometry available. [d] Reference 8. [e] Reference 7.

Ab initio[23] full geometry optimizations have been performed on silacyclopentadiene and diethynylsilane monomers, providing rather accurate theoretical estimates of the geometries and the ground-state energies of these molecules and also helping to assess the quality of the semiempirical PM3 calculations on the oligomers and polymers.

Table II. Experimental and MNDO PM3 Geometry[a] of (*exo*-Alkylidene)silacyclobutene Compounds[b]

	4a	4b	4c[c]	4d[c]
	exptl[d]	exptl[e]	MNDO PM3	MNDO PM3
Si–C(1)	1.906	1.86	1.883	1.855
Si–C(3)	1.915	1.88	1.889	1.878
C(2)–C(3)	1.500	1.51	1.473	1.477
C(1)–C(2)	1.367	1.40	1.343	1.345
C(3)–C(4)	1.334	1.35	1.317	1.319
C(1)–Si–C(3)	74.0	75.3	73.2	74.3
Si–C(1)–C(2)	91.9	92.8	92.5	92.4
C(1)–C(2)–C(3)	106.6	103.1	106.0	105.9
C(2)–C(3)–Si	76.5	88.7	88.3	87.4
C(2)–C(3)–C(4)		126.4	129.8	128.8

[a] Bond lengths are in angstroms and bond angles in degrees. Atom numbering is depicted in Figure 3. [b] **4a**, 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene (R1 = R2 = R3 = R5 = $SiMe_3$; R4 = R6 = Ph); **4b**, 4-alkylidene-1-silacyclobut-2-enyl ligand (R1 = R2 = Ph; R3 = CMe_3; R4 = Pt $(PEt_3)_2(H_2O)^+$; R5 = H; R6 = CMe_3); **4c**, 1,1-dimethyldiethynylsilane (R1 = R2 = Me; R3 = R4 = R5 = R6 = H); **4d**, diethynylsilane (R1 = R2 = R3 = R4 = R5 = R6 = H). [c] No experimental geometry available. [d] Reference 9. [e] Reference 10a.

III. Structure of Four- and Five-Membered Rings Containing Silicon

Crystal structure determinations of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene[8] (**3a**) and 1,1-dimethyl-2,4-diphenyl-1-silacyclopentadiene[7] (**3b**) have been published. Relevant bond lengths and angles are given, where available, in Table I. Figure 2 shows the atom numbering. In our MNDO PM3 calculations, for both molecules, the methyl and phenyl groups were fixed. The silole ring has C_{2v} symmetry, with the 2-fold axis bisecting the C(2)–C(3) bond and passing through the silicon atom.

The ring Si–C bond lengths deviate respectively for **3a** and **3b** from the experimental values by 0.000 and −0.006 Å, the central C—C single-bond length in the conjugated diene system by −0.028 and 0.000 Å and the C=C double bonds by −0.013 and −0.003 Å, respectively. The average deviation for bond angles from experiment within the ring is merely 0.4° for **3a** (no experimental bond angle values are available for **3b**). Phenyl rings are almost perpendicular to the silole ring, minimizing steric repulsions. Experimentally, the bulky groups in molecule **3a** increase bond lengths of the diene system, in comparison with bond lengths in **3b**. In molecule **3b**, the phenyl groups are nearly coplanar with the butadiene unit, while MNDO PM3 geometry predictions give almost perpendicular rings, underestimating the partial delocalization through the diene system and the heteroatom. Furthermore, for **3a**, PM3 calculations underestimate the difference between the $Si–C_{butadiene}$ bond length relative to the $Si–C_{methyl}$ bond length, giving a difference of +0.002 Å, as opposed to the experimental difference of +0.013 Å. PM3 also underestimates the $C–C_{phenyl}$ bond lengths relative to experiment by −0.023 Å for C(1)–C(7) and by −0.015 Å for C(2)–C(8). The study of molecule **3d** shows that in MNDO PM3 the Si–C length is underestimated when the substituent group of Si is hydrogen (R = H). Therefore, it is preferable to take an alkyl group as substituent for Si (R = Me for **1** and **2**). In conclusion, the MNDO PM3 method appears reliable to predict the geometry of silacyclopentadiene, except the well-known tendency of the MNDO method to give a cranky torsional angle between rings.[16b] Furthermore, the goal of these studies is to estimate the relative stability of polysilole and poly(diethynylsilane) via the relative heats of formation and E_g values, which are not significantly affected by this tendency (no bulky substituents on the diene system).

Only a few X-ray structures of (*exo*-alkylidene)silacyclobutenes have been published (**4a**[9] and **4b**[10]). We give the relevant bond lengths and angles of these compounds

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Table III. Geometry[a] of Silacyclopentadiene[b] and Diethynylsilane[b] Using ab Initio STO-3G and 6-31G* Basis Sets

	STO-3G	6-31G*		STO-3G	6-31G*
		Silacyclopentadiene **3d**			
Si–C(1)	1.849	1.876	C(1)–Si–C(4)	91.5	92.0
C(1)–C(2)	1.317	1.331	C(1)–C(2)–C(3)	115.7	117.9
C(2)–C(3)	1.512	1.497	Si–C(1)–C(2)	108.6	107.1
Si-H	1.423	1.477	H-Si-C(1)	113.9	114.1
			H-Si-C(1)-C(2)	117.1	117.6
		Diethynylsilane **4d**			
Si–C(1)	1.842	1.868	C(1)–Si–C(3)	74.5	74.4
Si–C(3)	1.860	1.891	C(1)–C(2)–C(3)	104.6	107.1
C(1)–C(2)	1.322	1.334	C(2)–C(3)–C(4)	130.7	130.0
C(2)–C(3)	1.506	1.487	C(1)–C(2)–Si	93.6	91.8
C(3)–C(4)	1.308	1.320	C(2)–C(3)–Si	87.2	86.7
Si–H	1.425	1.477	H–Si–C(1)	117.4	117.8
			H–Si–C(1)–C(2)	113.4	114.1

[a] Bond lengths are in angstroms and bond angles in degrees. Atom numbering is depicted in Figures 2 and 3. [b] Silacyclopentadiene **3d** and diethynylsilane **4d**: hydrogen substituents.

in Table II and compare them with MNDO PM3 geometries of the simplified rings of **4c** and **4d**. Because of the complex geometry of these four-membered rings, we can only verify the same trends as we have described above concerning the silole ring; a detailed comparison is not possible.

Also, we did ab initio calculations using the STO-3G and 6-31G* basis sets[23] for the five- and four-membered rings, with hydrogen taken as substituents (**3d** and **4d**, respectively). Structural parameters are summarized in Table III. It is interesting to note that the STO-3G minimal basis set is not very accurate in predicting the Si–C and Si–H bond lengths of a ring containing silicon. Bond lengths are underestimated, in order, by −0.024 Å for the Si—C bond and −0.034 Å for the C—C bond and overestimated by +0.024 Å for the C═C bond in comparison with bond averages of different experimental data for silacyclopentadiene. The corresponding values are +0.003, −0.020, and +0.009 Å for the 6-31G* basis set, respectively. The STO-3G basis set predicts a much shorter Si–H bond length (1.423 Å), while the 6-31G* basis set is quite good (Si–H = 1.485 Å in SiH_4). In conclusion, the double-ζ plus polarization basis set of 6-31G* gives reliable geometrical values for a ring containing silicon,[24] and the corresponding PM3 values are reasonable in comparison both to experiment and to the higher quality 6-31G* results.

IV. Theoretical Structure of Polysilole and Poly(diethynylsilane)

The repeat unit cells of the polymers under discussion are described in Figure 1. For polysilole, a C_2 axis intersecting the C(4)–C(5) bond and passing perpendicular through the backbone skeleton has been imposed. The methyl group substituents of silicon are fixed in both polymers. The silole ring and the four-membered ring are planar, with a free rotation along the C(4)–C(5) single bond in both polymers. Relevant bond lengths and angles are listed in Table IV. Before we compare these polymer data with those of the corresponding monomers, let us turn to an alternative analysis and compare the carbon skeleton of these polymers to that of polyacetylene (PA).

To analyze the geometrical perturbation of the PA-like skeleton due to heteroatom perturbations and ring constraints, we did MNDO PM3 calculations on polyacetylene isomers, corresponding to the carbon backbone conformation of **1** and **2**. These correspond to *all-trans*-polyacetylene (TT) and to *trans-cis-trans-transoid*-polyacetylene (TCTT), respectively. We have also studied the cis-transoid (CT) and trans-cisoid (TC) conformers. These regular polyacetylene isomers are shown in Figure 5, and the fully optimized geometrical values are listed in Table V.

Table IV. Geometry[a] of Polysilole 1 and Poly(diethynylsilane) 2 Using the MNDO PM3 Band Method

	Polysilole (R = Me)		
Si–C(1)	1.877	C(1)–Si–C(4)	93.2
C(1)–C(2)	1.350	C(1)–C(2)–C(3)	117.8
C(2)–C(3)	1.457	C(3)–C(4)–C(5)	125.6
C(4)–C(5)	1.432		
	Poly(diethynylsilane) (R = Me)		
Si–C(1)	1.903	C(1)–Si–C(4)	73.4
Si–C(3)	1.889	C(1)–C(2)–C(3)	107.2
C(1)–C(2)	1.354	C(2)–C(3)–C(4)	140.7
C(2)–C(3)	1.465	C(3)–C(4)–C(5)	126.2
C(3)–C(4)	1.334	C(5)–C(6)–C(7)	107.2
C(4)–C(5)	1.433	C(6)–C(7)–C(8)	131.8
C(5)–C(6)	1.356		
C(6)–C(7)	1.461		
C(7)–C(8)	1.332		

[a] Bond lengths are in angstroms and bond angles in degrees. Atom numbering is depicted in Figure 1.

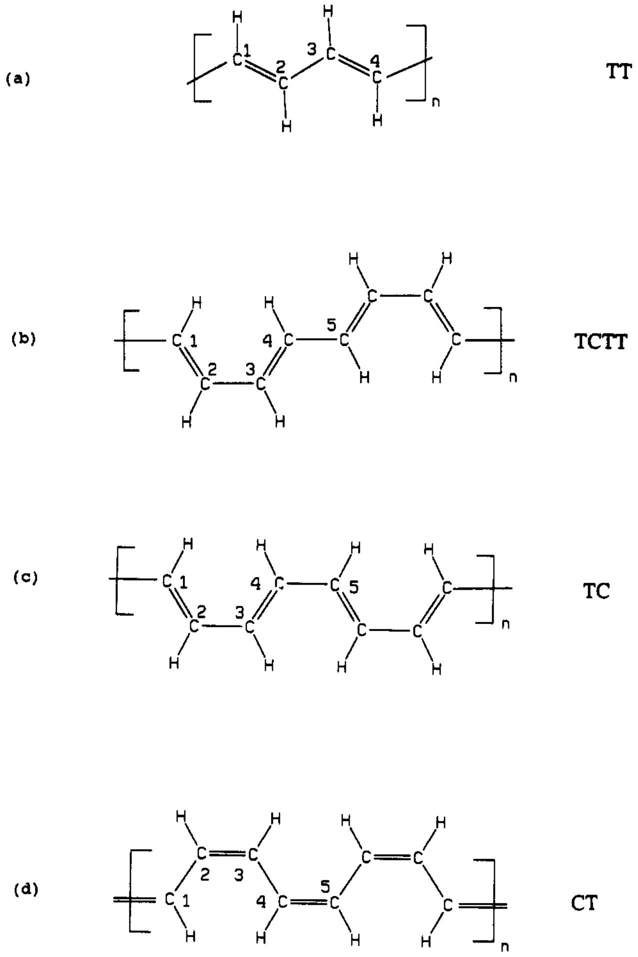

Figure 5. Polyacetylene (PA) isomers: (a) *all-trans*-PA (TT); (b) *trans-cis-trans-transoid*-PA (TCTT); (c) *trans-cisoid*-PA (TC); (d) *cis-transoid*-PA (CT).

Because of steric repulsions of the methyl groups, the adjacent silole rings are in an anti-planar conformation. In comparison with fully optimized TCTT polyacetylene,

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(24) (a) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419–7422. (b) Grigoras, S.; Lane, H. *J. Comput. Chem.* **1987**, *8*, 84–93.

Table V. Geometry[a] and Heat of Formation[b] of Polyacetylene Isomers[c] Using the MNDO PM3 Band Method

	TT Isomer		
C(1)–C(2)	1.344	C(1)–C(2)–C(3)	121.9
C(2)–C(3)	1.449	H–C(1)–C(2)	120.8
C(1)–H	1.098	H–C(2)–C(3)	117.3
	$\Delta H_f = 27.8$		
	TCTT Isomer		
C(1)–C(2)	1.345	C(1)–C(2)–C(3)	122.8
C(2)–C(3)	1.448	C(2)–C(3)–C(4)	122.8
C(3)–C(4)	1.345	C(3)–C(4)–C(5)	122.4
C(4)–C(5)	1.445	H–C(1)–C(2)	119.4
C–H	1.100	H–C(2)–C(3)	116.4
	$\Delta H_f = 28.2$		
	TC Isomer		
C(1)–C(2)	1.346	C(1)–C(2)–C(3)	123.1
C(2)–C(3)	1.446	H–C(1)–C(2)	119.3
C–H	1.102	H–C(2)–C(3)	117.5
	$\Delta H_f = 28.8$		
	CT Isomer		
C(1)–C(2)	1.449	C(1)–C(2)–C(3)	123.6
C(2)–C(3)	1.343	H–C(1)–C(2)	115.9
C–H	1.102	H–C(2)–C(3)	120.5
	$\Delta H_f = 29.0$		

[a] Bond lengths are in angstroms and bond angles in degrees. Atom numbering is depicted in Figure 5. [b] Heat of formation, ΔH_f, in kcal/mol of C_4H_4. [c] Polyacetylene isomers described in Figure 5.

Table VI. Heat of Formation[a] of Polysilole and Poly(diethynylsilane)

	n^b			
	1	2	3	poly ($n = 2$)
silole	8.3	20.5	32.6	24.3
diethynylsilane	28.1	54.6	82.1	54.0
$\delta(\Delta H_f)^c$	-19.8^d	−34.1	−49.5	−29.7

[a] Heat of formation, ΔH_f, in kcal/mol, using the MNDO PM3 method. [b] n = number of chemical repeating units, $C_4H_2SiMe_2$. [c] $\delta(\Delta H_f) = \Delta H_{f,\text{silole}} - \Delta H_{f,\text{diethynylsilane}}$. [d] The energy difference between **3d** and **4d** is −18.6 kcal/mol using the 6-31G* basis set and is −28.5 kcal/mol using the STO-3G basis set.

Table VII. Calculated Band Gap E_g^{scaled} for Polysilole 1, Poly(diethynylsilane) 2, and Polyacetylene TCTT and TT Conformations

	1	PA backbone of 1[c]	PA TCTT[d]
HOCO[a]	−11.10	−11.10	−11.16
$E_g^{\text{scaled }b}$	1.44	1.29	1.52
	2	PA backbone of 2[c]	PA TT[d]
HOCO[a]	−11.23	−11.23	−11.21
$E_g^{\text{scaled }b}$	1.99	1.99	1.80

[a] Highest occupied level energy, in eV, based on EHT band calculations using MNDO PM3 geometry. [b] Energy band gaps, in eV, have been determined using the scale factor *k* defined in the text. [c] EHT calculations based on the MNDO PM3 geometry of polysilole and poly(diethynylsilane). $SiMe_2$ is replaced by two H atoms. [d] EHT calculations based on MNDO PM3 geometry of fully optimized TCTT and TT polyacetylene.

in the diene system **1** with rings there is a reduction of the C(1)–C(2)–C(3) angle by 5° relative to TCTT polyacetylene. The nonbonding H···H repulsions in polyacetylene also tend to increase this angle. For the same reason, the exo single bond C(4)–C(5) decreases by −0.013 Å in polysilole relative to TCTT PA. Bond lengths in **1** increase overall relative to those in PA by +0.006 Å for C(1)–C(2) and by +0.008 Å for C(2)–C(3), which indicate little delocalization through the heteroatom. In conclusion, the formation of the five-membered ring by connection of the $SiMe_2$ groups in **1** perturbs the carbon skeleton only slightly relative to that in *trans-cis-trans-transoid*-polyacetylene.

The comparison between monomer **3c** and polysilole **1** shows some delocalization along the adjacent π-systems: the double bond C(1)–C(2) increases by +0.014 Å and the single bond C(2)–C(3) decreases by −0.014 Å. The Si–C bond length increases by +0.021 Å, which is of the same order as the change in the monomer upon substitution by phenyl groups in the α-position (**3b**).

The major feature of the poly(diethynylsilane) structure **2** is the high-strain geometry due to the four-membered rings. Double and single bonds of the carbon skeleton of **2** differ significantly, depending upon whether they are exo or endo bonds: the exo bonds are shorter by −0.022 Å for the double bonds and by −0.030 Å for the single bond. It is worthwhile to note that the average C—C and C═C bond lengths, 1.344 and 1.450 Å, respectively, for **2**, are very close to their corresponding values in *all-trans*-polyacetylene. The bond angles, of course, differ considerably. The differences and similarities of the electronic properties of **2** and *all-trans*-polyacetylene could be largely attributed to these features. Finally, we compare the structures of the monomer **4c** and the polymer **2**: delocalization along the π-system increases the double-bond lengths and decreases the single bonds, similar to the case described above for polysilole.

In conclusion, we found that the carbon backbones of poly(silacyclopentadiene) and poly(diethynylsilane) are very similar to the corresponding conformations of polyacetylene, the differences being related to ring formation. This difference relative to PA is larger for **2** due to the larger ring strain of the four-membered ring. This leads to the differences of stability and E_g, as well be discussed in the next section.

V. Polysilole or Poly(diethynylsilane)?

The difference in stability of the two isomers polysilole and poly(diethynylsilane) has been estimated using the MNDO PM3 method. Calculations have been done for mono-, di-, tri-, and polymers for each isomer. The heat of formation values are listed in Table VI. As expected, the results indicate clearly that the five-membered-ring polysilole structure is more stable by about 15 kcal/mol per chemical repeating unit than poly(diethynylsilane). As mentioned before, the strained geometry of structure **2** destabilizes the ring system. Ab initio calculations on the monomers provide the same conclusion: silacyclopentadiene is more stable by 18.6 kcal/mol at the 6-31G* basis set level and by 28.5 kcal/mol at the STO-3G basis set level. On the basis of these energy data, polysilole should be more stable than poly(diethynylsilane), which is believed to be the form synthesized by Wong et al.[2] However, it is conceivable that polysilole can also be made: Ishikawa et al.[25] have reported that a nickelasilacyclobutene on reaction with an acetylenic compound gave both five- and four-membered (**4a**) rings, in 32% and 6% yields, respectively. Let us turn now to the issue of optical absorption and band gap.

As mentioned in the Methodology section, scaled band gap values, E_g^{scaled}, have been calculated as $E_g^{\text{scaled}} = kE_g^{\text{EHT,PM3}}$ and will be compared to experimental values. Our prediction for E_g^{scaled} of poly(diethynylsilane) (1.99 eV) is in good agreement with the experimental value (2.0 eV).[2] This value is larger by 0.55 eV than that of polysilole. Further details concerning energy gaps and the highest

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(25) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* 1986, 108, 7417–7419.

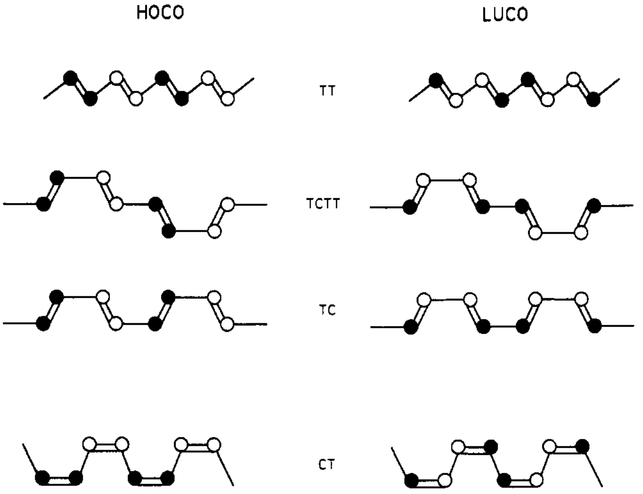


Figure 6. Orbital patterns of the highest occupied (HOCO) and the lowest unoccupied (LUCO) crystal orbitals for each PA isomer. The polymer skeletons are the same as those shown in Figure 5.

occupied crystal orbital (HOCO) energy are summarized in Table VII.

For a class of heterosubstituted conjugated polymers, the energy gap can be described by

$$E_g \approx E_g^{\mathrm{Peierls}} + E_g^{1-3} + E_g^{1-4} + E_g^{\mathrm{non\text{-}plan}} + E_g^{\mathrm{heteroatom}} \tag{3}$$

where $E_g^{\mathrm{Peierls}} \approx c\delta r$ is the contribution caused by bond length alternation,[12b,c] E_g^{1-3} is the contribution arising from second-neighbor interactions and depends on the CCC bond angles and δr in the PA-like skeleton, E_g^{1-4} is the contribution arising from third-neighbor interactions and depends on the ring geometry and conformation,[12e] $E_g^{\mathrm{non\text{-}plan}}$ depends on the planarity of the system,[12d] and $E_g^{\mathrm{heteroatom}}$ arises from heteroatom energy level shifts due to a destabilization or stabilization of ring orbitals.[12d] The average bond alternation is $\delta r = \sum^n r_{\mathrm{C-C}}/n - \sum^n r_{\mathrm{C=C}}/n$, where n is the number of C–C single bonds (or double bonds) in the PA-like skeleton of the polymer.

Formula 3 can be derived on the basis of first-order perturbation theory[19] in which the effects of different perturbations are additive.

For polymers **1** and **2** and polyacetylene isomers, $E_g^{\mathrm{non\text{-}plan}}$ and $E_g^{\mathrm{heteroatom}}$ do not contribute to the energy gap, because (i) the backbone is planar for all studied polymers and (ii) for **1** and **2** both the π HOCO and the π^* LUCO (lowest unoccupied crystal orbital) do not significantly mix with the 3p silicon orbitals, because they are in an approximately sp^3 hybrid state. The density of states of poly(diethynylsilane) and polysilole showed clearly that the silicon contribution does not affect the π and π^* levels significantly. The effect of Si π orbitals on the HOCO and LUCO are smaller for **2** than for **1**: Si π orbitals of **2** cannot mix well with the corresponding carbon π orbitals, because they have opposite signs (C(1) and C(2)). This mixing is allowed for **1** by symmetry, as shown in Figure 6. This explains the slight difference listed in Table VII between the gap of **1** (1.44 eV) and that of the corresponding PA backbone (1.29 eV).

The energy gap of polysilole, poly(diethynylsilane), and polyacetylene isomers can be explained by taking into account the alternation δr of long and short C–C bonds along the carbon backbone and by the 1–3 and 1–4 orbital interactions. The calculated band gap and bond alternation values are listed in Table VIII. Let us focus our discussion on four polyacetylene isomers and on polysilole and poly(diethynylsilane). As Table VIII indicates, the bond alternation cannot explain alone the differences of energy gaps of these carbon backbone isomers. This follows from the nature of the HOCO and LUCO orbitals, which are given in Figure 6. The effects of second- and third-neighbor interactions are illustrated in Figure 7 for **1** as derived from the TCTT conformation of PA and for **2** as derived from the TT conformation of PA. The difference of the band gap of 0.19 eV between the two TT backbones (Figure 7b) comes from 1,3-interactions ($E_g^{1,3}$) due to differences in C–C–C bond angles and δr variations. The difference of 0.13 eV between the two TCTT back-

Table VIII. Bond Alteration[a] and Energy Band Gap[b]

	polymer					
	TT	TCTT	TC	CT	1	2
δr	0.105	0.102	0.100	0.106	0.095	1.106
E_g^{scaled}	1.80	1.52	1.29	2.18	1.44	1.99

[a] Bond alteration, in angstroms. [b] Energy band gaps, in eV, using the scale factor k defined by eq 2.

Table IX. Geometry[a] and Electronic Structure of the Linear $[\mathrm{C_4SiMe_2}]_n$ Polymer 5

C(1)–C(2)	1.200	C–Si–C	109.14
C(2)–C(3)	1.369	C(1)–Si–$\mathrm{C_{Me}}$	109.34
Si–C(1)	1.757	$\tau_{\mathrm{Si-C_{Me}}}$	60.38
Si–$\mathrm{C_{Me}}$	1.894		
HOCO[b]	−12.26		
$E_g^{\mathrm{scaled}\,c}$	7.60		

[a] Bond lengths are in angstroms and bond and dihedral (τ) angles in degrees, calculated using the MNDO PM3 band method. Atom numbering is depicted in Figure 10. [b] Highest occupied level energy, in eV, based on EHT band calculations using the MNDO PM3 geometry. [c] The band gap, in eV, has been determined using the scale factor k defined by eq 2.

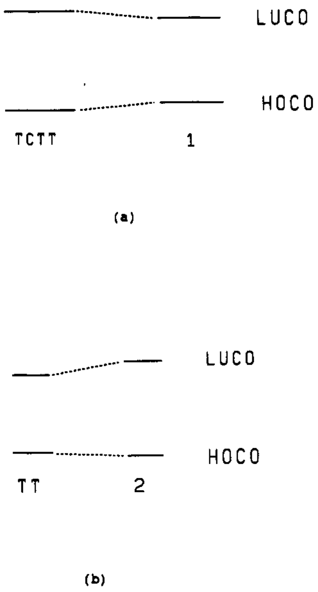


Figure 7. Effects of third atomic neighbor E_g^{1-4} and second atomic neighbor E_g^{1-3} contributions on the energy gap for (a) **1** vs TCTT and (b) **2** vs TT.

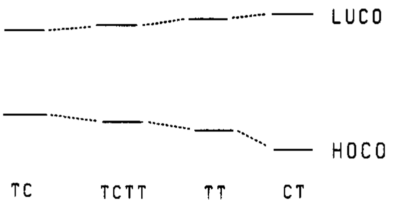
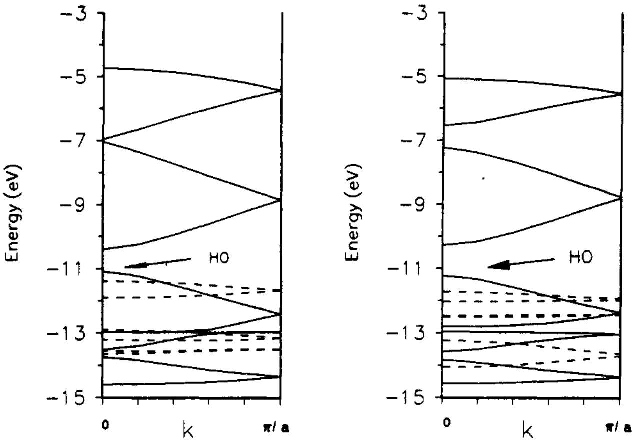
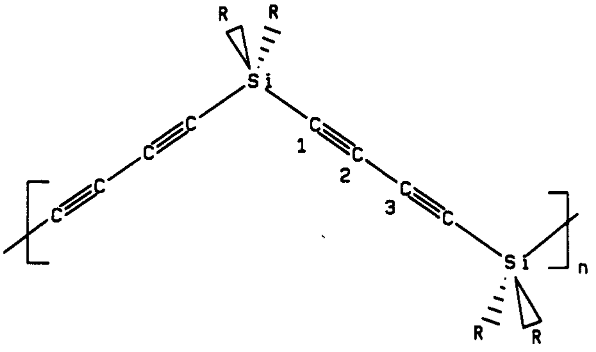


Figure 8. Effects of third atomic neighbor E_g^{1-4} and second atomic neighbor E_g^{1-3} contributions on the energy gap for polyacetylene isomers.



a) b)

Figure 9. Band structures of (a) polysilole and (b) poly(diethynylsilane). The solid lines are the π bands, and the dashed lines are the σ bands. HO is the highest occupied level.



5

Figure 10. Structure of the linear $[C_4SiMe_2]_n$ polymer 5.

bones (Figure 7a) is due to 1,3-interactions, because of the distortion of the skeleton due to the presence of five-membered rings.

A comparison of the four main conformations of PA is shown in Figure 8, where only the $E_g^{1,4}$ contributions to the gap change significantly. For the $E_g^{1,4}$ contribution within a unit cell of polysilole (or TCTT), the comparison with the corresponding contribution of poly(diethynylsilane) (or TT) indicates that the HOCO of 1 is less stable than the HOCO of poly(diethynylsilane) (or TT), but the LUCO is more stable than the LUCO of poly(diethynylsilane) (or TT). This is the main reason for the smaller band gap of 0.55 eV in polysilole relative to the band gap of poly(diethynylsilane). The corresponding difference between the gaps of TCTT and TT conformations of PA is very similar, 0.49 eV.

Another important feature of the electronic structure is the bandwidth of the HO and LU bands. These are around 5 eV for TT polyacetylene and 2.5 eV for TCTT polyacetylene.[19] From their band structures (Figure 9), both 1 and 2 are very similar to polyacetylene and therefore both are good candidates for high intrinsic conductivity.

We have calculated also the geometric and electronic structure of the linear $[C_4SiMe_2]_n$ polymer 5, as depicted in Figure 10. The geometry and electronic properties are listed in Table IX. This linear structure 5 has a calculated energy gap which is much larger than the analogous polymers containing rings (1 and 2). Our calculated gap value may be somewhat overestimated, because k has been determined for the polymers containing a PA-like backbone, which obviously is not present for model 5. Tanaka et al. have studied several π-conjugated Si linear polymers.[26] The energy gap values of the linear Si polymers investigated by Tanaka et al. have calculated energy gap values ranging from 3.8 to 5.3 eV, which qualitatively agree with the corresponding experimental gaps ranging from 4.8 to 5.3 eV, where data are available.[27] The bandwidths of 5 are about 0.5 eV (see Figure 11) and are much smaller than for 1 and 2; thus, this linear form is not as good a candidate for high intrinsic conductivity. The unoccupied σ-bands shown in Figure 11 are all approximately in-plane (cumulene-type) π-orbitals. For the occupied σ-levels such a distinction can be made for a few bands, but these mix significantly with the Si σ-orbitals.

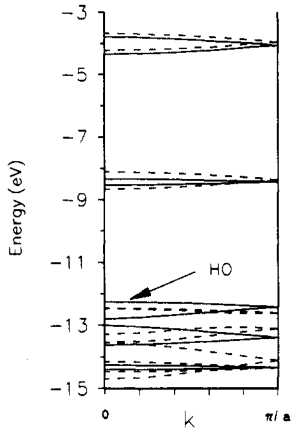


Figure 11. Band structures of the linear $[C_4SiMe_2]_n$ polymer 5. The solid lines are the π bands, and the dashed lines are the σ bands. HO is the highest occupied level.

Under different reaction conditions $R_2Si(C{\equiv}CH)_2$ monomers were polymerized by catalysis, and it appears that the polymers obtained may have three different structures: one of them is linear,[5,28] the second one is the five-membered-ring polymer 1, polysilole, and the last one is the four-membered-ring polymer 2, poly(diethynylsilane). Considering the energy band gap, the linear structure 5 cannot be confused with the polymers containing rings. Our calculations also show that even though 1 is more stable than 2 by 15 kcal/mol per chemical unit, only structure 2 is consistent with the optical absorption spectrum of the sample synthesized by Wong et al.[2] The synthesis of polysilole could lead to an interesting new electronic material.

Acknowledgment. G.F.'s stay at Georgetown University has been supported by the Conseil Regional de Bretagne. We thank the National Science Foundation for generous support (Grant No. DMR9115548) and the U.S. Air Force Office of Scientific Research for Grant No. AFOSR-89-0229. We are grateful to John Akapulco for the drawings.

Registry No. $Me_2Si(C{\equiv}CH)_2$ (homopolymer), 29464-10-6; $Bu_2Si(C{\equiv}CH)_2$ (homopolymer), 134490-63-4; $Ph_2Si(C{\equiv}CH)_2$ (homopolymer), 52016-42-9.

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