2220 (w), 2200 (w), 2120 (w), 1435 (m), 1360 (w), 1255 (w), 1215 (w), 1160 (m), 1085 (w), 1020 (vs, br), 918 (m), 882 (m), 835 (w), 750 (s), 720 (s), 680 (m) cm^{-1}.

4-Methyl-d_3-benzyl Alcohol (17c). Following the same procedure as for **17a**, using LAH (244 mg, 5.89 mmol) and **16c** (1.95 g, 11.7 mmol), we obtain via recrystallation from heptane **17c** as white needles (872 mg, 61.9%): mp 56 °C (lit. 59-60 °C); NMR (CDCl$_3$) δ 1.6 (s, 1 H), 4.6 (s, 2 H), 7.3 (s, 4 H); IR (neat) 3360 (s, br), 3090 (w), 3050 (m), 3010 (m), 2930 (m), 2870 (m), 2230 (w), 2205 (w), 2170 (w), 2050 (w), 1617 (w), 1518 (s), 1460 (m), 1418 (s), 1370 (w), 1205 (m), 1180 (w), 1025 (vs), 1015 (vs), 885 (s), 775 (s), 718 (s), 675 (w) cm^{-1}.

2-Methyl-d_3-Benzyl Bromide (7). Following a procedure similar to the one used in the conversion of **13a** to **14a**, using phosphorus tribromide (960 mg, 3.54 mmol) and **17a** (640 mg, 5.11 mmol), we obtained via Kugelrohr distillation (80 °C (3 mm)) **7** as water white liquid which solidified on standing (512 mg, 77%): NMR (CDCl$_3$) 4.5 (s, 2 H), 7.2 (s, 4 H); IR (neat) 3060 (m), 3020 (s), 2975 (m), 2925 (m), 2865 (m), 2225 (m), 2205 (m), 2120 (w), 2070 (w), 2050 (w), 1605 (m), 1578 (m), 1490 (s), 1452 (s), 1442 (s), 1375 (w), 1299 (w), 1282 (m), 1235 (m), 1215 (vs), 1193 (s), 1160 (w), 1135 (w), 1085 (m), 1045 (m), 945 (m), 892 (w), 875 (w), 837 (m), 755 (vs), 715 (m), 685 (s), 600 (s), 582 (m) cm^{-1}.

3-Methyl-d_3-benzyl Bromide (8). Following the same procedure as for **7**, using phosphorus tribromide (913 mg, 3.37 mmol) and **17b** (616 mg, 4.87 mmol), we obtained via Kugelrohr distillation (80 °C (2.5 mm)) **8** as a water white liquid: NMR (CDCl$_3$) δ 4.4 (s, 2 H), 7.2 (s, 4 H); IR (neat) 3100 (w), 3035 (w), 3020 (m), 2875 (w), 2230 (w), 2210 (w), 2130 (w), 2060 (w), 1608 (m), 1588 (w), 1485 (m), 1440 (m), 1265 (m), 1212 (s), 1165 (w), 1082 (m), 1050 (w), 922 (m), 905 (w), 835 (w), 760 (s), 715 (m), 690 (s), 605 (s), 558 (w) cm^{-1}.

4-Methyl-d_3-benzyl Bromide (6). Following the same procedure as for **7**, using phosphorus tribromide (474 mg, 1.74 mmol) and **17c** (431 mg, 3.45 mmol), we obtained via Kugelrohr distillation (80 °C (3.5 mm)) **6** as a water white liquid which solidified on standing (436 mg, 68%): NMR (CDCl$_3$) δ 4.2 (s, 2 H), 7.05-7.4 (A_2B_2, $\delta(H_A)$ 7.34, $\delta(H_B)$ 7.13, J_{AB} = 9 Hz, 4 H); IR (neat) 3130 (w), 3090 (w), 3050 (m), 3030 (m), 3005 (m), 2870 (w), 2230 (q), 2210 (w), 2130 (m), 2050 (m), 1915 (w), 1615 (m), 1515 (s), 1439 (m), 1415 (s), 1225 (vs), 1205 (s), 1185 (w), 1105 (w), 1045 (w), 1018 (w), 950 (w), 890 (s), 828 (m), 785 (s), 708 (s), 682 (s), 595 (m) cm^{-1}.

Silabutadienes and Their Silylene Isomers. An ab Initio Study

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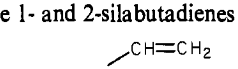
Contribution from the Laboratoire de Physique Quantique (E.R.A. 821), Université Paul Sabatier, 31062 Toulouse Cedex, France. *Received March 18, 1981*

Abstract: 1-Silabutadiene (**1**), 2-silabutadiene (**2**), and their respective singlet silylene isomers allylsilylene (**3**) and methylvinylsilylene (**4**) are investigated through ab initio double ζ + d(Si) SCF calculations. The calculated SCF relative stabilities (**4** < **2** < **1** < **3**) should be modified by correlation effects to the **2** < **4** < **1** < **3** ordering. π-Conjugation in silabutadienes is put in evidence through an analysis of energy shifts and π charge transfers which are predominantly Si=C→C=C in **1** while C=Si←C=C in **2**. This conjugation strongly stabilizes 1-silabutadiene (**1**) with respect to its silylene isomer **3**, while the conjugation in **2** is balanced by the $\pi_{C=C} \rightarrow 3p_{zSi}$ delocalization occurring in **4**.

I. Introduction

The field of theoretical stability of π-bonded silicon compounds has been substantially explored. Since the previous works of Gordon[1] and Strausz et al.,[2] many ab initio calculations using extended basis sets and including CI have appeared (for reviews, see ref 3 and4). A general feature in organosilicon unsaturated compounds is that the preferred forms are cycles (when possible) or silylenes rather than silico olefin forms. The simplest case, silaethylene, which bears one unsaturation on two centers, has been studied extensively.[5-7] Goddard's most reliable results concerning the (lower) singlet states predict silaethylene to lie only 0.4 kcal/mol above methylsilylene.[7] The next series concerns three centers and one unsaturation, namely, C_2SiH_6; Gordon's SCF calculations[6] predict the preferred forms to be dimethylsilylene and silacyclopropane (apart from the stable vinylsilane in which the silicon atom is not involved in the unsaturation). Barthelat et al.[8] have explored the case of two unsaturations on three centers (C_2SiH_4) showing the most stable isomers were silacyclopropylidene and silacyclopropene. The C_3SiH_4 isomers correspond to three unsaturations on four centers; Gordon[9] has calculated silacyclobutadiene to be more stable than silatetrahedrane, as for carbon analogues. An interesting series deals with two unsaturations on four centers, allowing conjugation of a Si=C bond with a C=C bond. One may wonder whether the conjugation in silabutadienes could stabilize the Si=C bonds with respect to the silylene forms. In the literature is actual mention of the occurrence of transient 1-silabutadienes[4] and 2-silabutadienes.[4,10,11]

This work is an ab initio study, mainly at the SCF level, of the stability and electronic structure of some C_3SiH_6 isomers limited to the 1- and 2-silabutadienes (**1** and **2**) and to their corresponding



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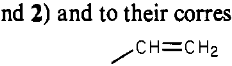

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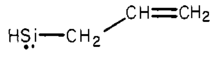

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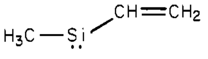

4

linear silylene isomers, namely, allylsilylene (**3**) and methylvinylsilylene (**4**).

Calculations on silaethylene, methylsilylene, and vinylsilylene are also reported which allow (i) comparisons with other all electron calculations, (ii) geometrical assumptions, and (iii) an estimate of possible correlation effects in **1** to **4**.

II. Computational Details

All the SCF results reported here are obtained from the PSHONDO algorithm[12] which introduces the pseudo-potentials of Durand and Barthelat[13] into the HONDO program.[14] For carbon

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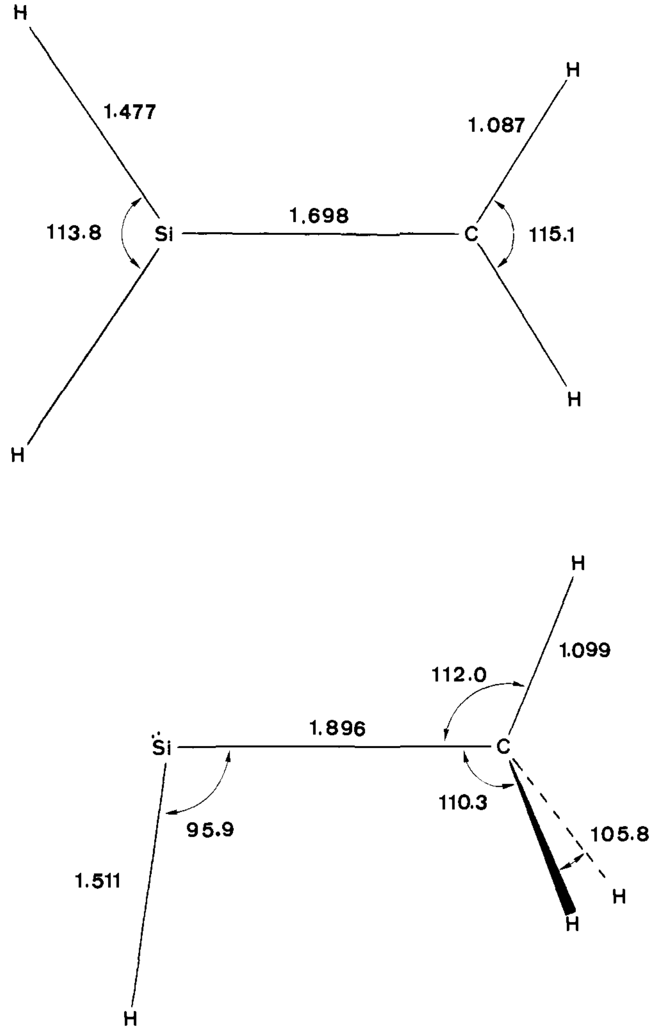

Figure 1. SCF calculated equilibrium geometries of silaethylene (top) and singlet methylsilylene (bottom), in angstroms and degrees.

and silicon atoms valence basis sets are optimized in a pseudopotential SCF calculation of the ground state of the atom using a quadruple ζ Gaussian basis set. These four Gaussian functions are contracted to the double ζ (DZ) level by means of a 3 + 1 procedure for C and a 2 + 2 procedure for Si. For silicon a 3d Gaussian function was added as a polarization function, the orbital exponent of which was optimized on SiH_4 ($\eta_d = 0.45$). Moreover, some calculations on $H_2Si{=}CH_2$ and $H\ddot{S}i{-}CH_3$ include a d Gaussian function on the carbon atom ($\eta_d = 0.7$). The details of the pseudo-potential parameters and optimized basis sets are available upon request. On silaethylene and methylsilylene, extended CI's were carried out according to the CIPSI algorithm.[15,16] A variational zeroth-order wave function is built from an interative selection of the most important determinants, the other ones being taken into account through a second-order Möller–Plesset perturbation. The determinants having a coefficient larger than 0.025 in the first-order wave function of the ground-state determinant have been included in the zeroth-order variational wave function at the final step; as a typical example, for silaethylene, 34 determinants were included in the variational wave function, from which single and double substitutions generate 3 × 10^5 determinants, all of them being treated by a second-order Möller–Plesset-type perturbation expansion.

The geometrical parameters were optimized independently except for strongly dependent parameters such as two valence angles on the same center, where dependent optimizations were carried out.

Table I. SCF and CI Results on the Si=C Bond in Silaethylene (DZ + d(Si and C) Basis Sets)

	SCF	CI
$d_{Si=C}$, Å	1.690	1.722
$k_{Si=C}$, mdyn/Å	6.38	5.14
$\nu_{Si=C}$, cm^{-1}	1064	955

Table II. Relative Energies E(silaethylene) − E(methylsilylene), in kcal/mol (DZ + d(Si and C) Basis Sets)

	all electron		pseudo-potential
	Gordon[a]	Goddard[b]	this work[c]
SCF	5.23	4.9	1.51
CI	−2.1[d]	0.4[e]	−3.49[f]

[a] Reference 6. Geometries optimized at the DZ level (3.21 G). [b] Reference 7. Geometries optimized at the DZ level. [c] Geometries optimized at the DZ + d(Si) level. [d] Möller–Plesset second-order perturbation corrections. [e] Large-scale CI. [f] Large-scale CI (CIPSI).

III. Silaethylene and Methylsilylene

The geometries of singlet silaethylene and methylsilylene were fully optimized at the DZ (+d on Si) level. The results are reported in Figure 1. They compare well with Goddard's results[7] although our Si–C bond lengths are shorter owing to inclusion of d orbitals on silicon in the geometry optimization. Because of a discrepancy between most of the quantum-calculated Si=C bond lengths ($\simeq$1.70 Å) and a recent electron-diffraction experimental value on $Me_2Si{=}CH_2$ (1.83 Å),[17] the Si—C bond in silaethylene has been studied further on by including d orbitals on the carbon atom and by optimizing it at the extended CI level. The results reported in Table I show that d AO's on the carbon atom shorten the Si=C bond length by 0.01 Å while the CI only lengthens it to 1.72 Å. Hence the difference between the SCF calculated and electron-diffraction-measured Si—C bond lengths is not due to correlation effects. Through MINDO/3 calculations[18] the Si=C bond length in silaethylene has been estimated to lengthen by 0.04 Å under Si dimethylation. (In the carbon series, when going from ethylene to isobutene, the experimental change in the C=C bond length is only a $\simeq$0.01-Å shortening). The discrepancy 1.83 Å vs. $\simeq$1.70 Å can hardly be explained by substituent-effect considerations. CI induces a 109-cm^{-1} decrease of the (uncoupled) Si=C vibrator frequency. The resulting CI calculated $\nu_{Si=C}$ on silaethylene (955 cm^{-1}) supports recent experimental assignments of the 1001-[19] or 1003-cm^{-1}[20] band in the IR spectra of 1,1-dimethyl 1-silaethylene.[21] Our CI $k_{Si=C}$ force constant compares well with the value obtained from experiment on $Me_2Si{=}CH_2$ using force-field calculations (5.6 mdyn/Å).[20] As regards force constants, our results do not support the recently proposed[20,22] similarity between silaethylene and phosphonium ylide.[23]

At the SCF DZ + d(Si and C) level, silaethylene lies only 1.51 kcal/mol above methylsilylene (see Table II). The extended CI brings a 134.4-kcal/mol valence correlation energy on $H_2Si{=}CH_2$ compared with 129.4 kcal/mol on $H\ddot{S}i{-}CH_3$. The energy dif-

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(20) Nefedov, O. M.; Maltsev, A. K.; Khabashesku, V. N.; Korolev, V. A. *J. Organomet. Chem.* **1980**, *201*, 123.

(21) In the carbon series, the effect of dimethylation from ethylene to isobutene results in a 30-cm^{-1} increase of stretching $\nu_{C=C}$.

(22) Nefedov, O. M.; Maltsev, A. K.; Khabashesku, V. N. *Angew. Chem.*, in press.

(23) At the SCF DZ + d(Si or P) level, the calculated $k_{Si=C}$ force constant in $H_2Si{=}CH_2$ (6.6 mdyn/Å) differs significantly from the calculated $k_{P=C}$ force constant in $H_3P{=}CH_2$ (5.7 mdyn/Å: Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7169).

Table III. Optimized Central Bond Lengths with Corresponding Force Constants for 1, 2, and Butadiene[a]

	1	2	$H_2C{:}CHCH{:}CH_2$	$H_2C{=}CH_2$	$H_2Si{=}CH_2$	$H_3Si{-}CH{:}CH_2$
d, Å	1.476	1.845	1.475	1.333	1.698	1.868
k, mdyn/Å	6.1	3.9	6.3	10.7	6.6	3.5

[a] Ethylene, silaethylene, and vinylsilane are included for comparison.

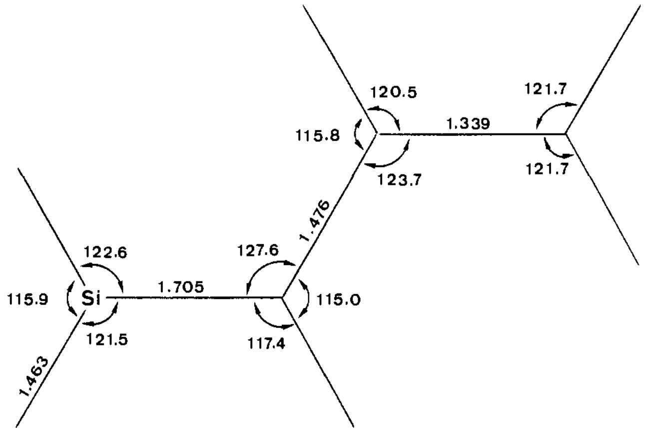


Figure 2. Optimized geometrical parameters for 1-silabutadiene (**1**), in angstroms and degrees.

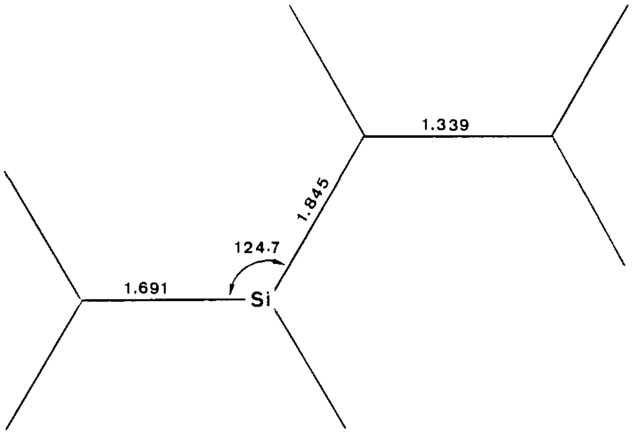


Figure 3. Optimized geometrical parameters for 2-silabutadiene (**2**), in angstroms and degrees.

ference after CI is therefore 3.5 kcal/mol in favor of silaethylene. Table II compares these results with the best calculations of Gordon[6] and Goddard et al.[7] At the SCF level, the difference between their results (≃5 kcal/mol) and ours (≃1.5 kcal/mol) may come from the DZ + d geometries (this work) vs. the DZ geometries.[6,7] The difference of correlation energies, in favor of silaethylene (5.0 kcal/mol), is comparable with the previous works (7.3[6] and 5.3[7] kcal/mol). One can note that this 5.0-kcal/mol correlation energy difference is mainly given by the specific valence contributions $(\pi \rightarrow \pi^*)^2$ in $H_2Si{=}CH_2$ and $(n_\sigma \rightarrow p_{\pi Si})^2$ in $H\ddot{S}i{-}CH_3$, the difference of which is 6.9 kcal/mol. The main conclusion of these results is that singlet silaethylene and methylsilylene lie close in energy.

IV. Silabutadienes and Their Silylene Isomers. Results

A. Geometries. The geometries were not fully optimized for all compounds **1**–**4**. The main geometrical parameters were optimized while the other were taken from model compounds $H_2Si{=}CH_2$, $H\ddot{S}i{-}CH_3$, $H_2C{=}CH_2$, and $H\ddot{S}i{-}CH{=}CH_2$. 1-Silabutadiene and allylsilylene were more extensively optimized, allowing for a further check of the geometrical assumptions.

1-Silabutadiene (1). Noticing that in butadiene the $H_2C{=}CH$- fragments almost keep ethylene geometry, the optimized ethylene (CC = 1.333 Å, CH = 1.083 Å, and ∠-HCH = 116.3°) and silaethylene (see Figure 1) geometries were introduced as a starting point for 1-silabutadiene and all the geometrical parameters (except CH bond lengths) were optimized in the s-trans planar conformation. The optimized parameters are reported in Figure 2. One can see that the use of silaethylene and ethylene geometries as the $H_2Si{=}CH$- and $-CH{=}CH_2$ fragment geometries in **1** is a reasonable assumption. The energy obtained from this guess and an optimization of four basic parameters only ($Si{=}C_2$, $C_2{-}C_3$, and $C_3{=}C_4$ bond lengths and ∠ SiC_2C_3 angle) is only 0.4 kcal/mol above the fully optimized geometry value. The Si=C bond is 0.007 Å longer than in silaethylene, the C=C bond is 0.006 Å longer than in ethylene, and the central C—C bond length is nearly the same as that calculated in butadiene, 1.475 Å.

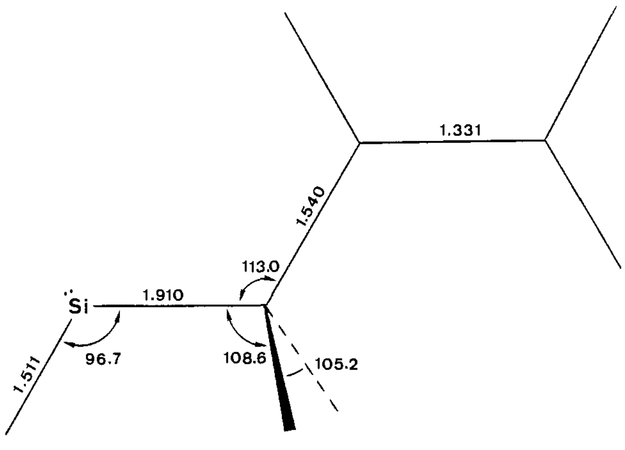


Figure 4. Optimized geometrical parameters for allylsilylene (**3**), in angstroms and degrees.

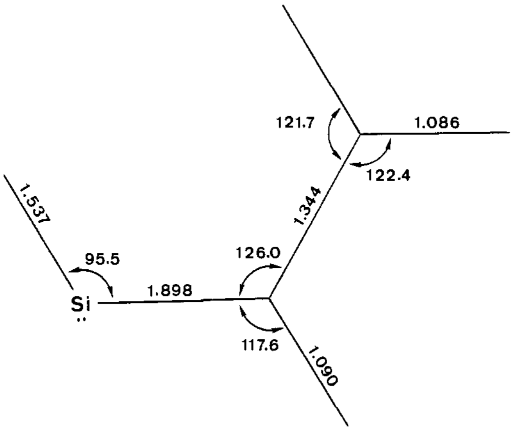


Figure 5. Calculated equilibrium geometry of vinylsilylene, in angstroms and degrees.

2-Silabutadiene (2). In view of the preceding remarks, the geometry optimization was restricted to the four main geometrical parameters, the remainder being derived from silaethylene and ethylene geometries. They are reported in Figure 3. A comparison of the central bond lengths with corresponding force constants in **1**, **2**, butadiene, and vinylsilane which were computed for comparison is made in Table III. As an indication of conjugation in **2**, on may notice the Si–C central bond length shortening (0.02 Å) with respect to vinylsilane which only presents a p_π–d_π conjugation. The force constants parallel this observation as well as the π-overlap populations (vide infra).

Allylsilylene (3). A C_s s-trans form was kept. The optimized parameters are reported in Figure 4. No great difference with methylsilylene appears except for the Si–C distance which is ≃0.01 Å longer in **3**.

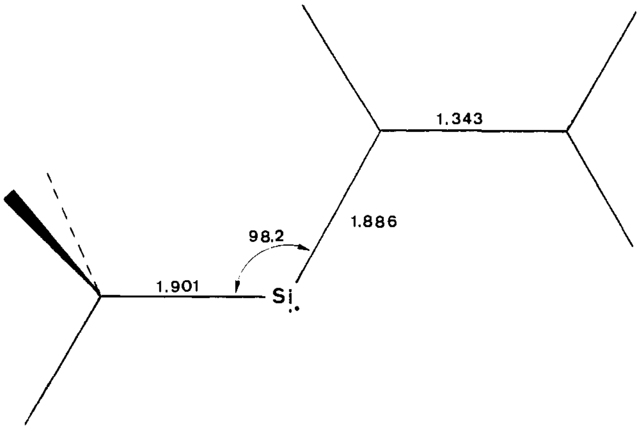


Figure 6. Optimized geometrical parameters for methylvinylsilylene (**4**), in angstroms and degrees.

Table IV. Relative Energies (in kcal/mol) of Silabutadienes and Linear Silylenes[a]

	SCF calcd		after correlation estimation
$CH_3\underset{..}{Si}CH=CH_2$ (4)	0		5
$CH_2=SiHCH=CH_2$ (2)	2.18	5.83	0
$SiH_2=CHCH=CH_2$ (1)	8.01	8.91	6
$H\underset{..}{Si}CH_2CH=CH_2$ (3)	16.92		22

[a] E_0^{SCF} corresponds to −23.620 65 au valence total energy.

Methylvinylsilylene (4). The simpler vinylsilylene molecule was fully optimized first. The result is reported in Figure 5. Starting from the vinylsilylene and methylsilylene geometries for each fragment, the main parameters were optimized in **4** which was assumed C_s and s-trans. They are given in Figure 6. One can note a 0.01-Å shortening of the Si–C_{sp^2} bond length owing to an expected $\pi_{C=C} \rightarrow 3p_{zSi}$ conjugation.

B. Energies. The relative SCF energies are reported in Table IV. The main results are (i) 2-silabutadiene is more stable than 1-silabutadiene (by 6 kcal/mol), (ii) 1-silabutadiene is more stable than its silylene form **3** (by 9 kcal/mol), but (iii) 2-silabutadiene is less stable than its silylene form **4** (by 2 kcal/mol).

It may be worthwhile to give an estimation of the correlation corrections to the SCF relative energies of **1** to **4** using the CI results on silaethylene and methylsilylene. Assuming a partition of correlation energy into bond contributions, one may suppose that the correlation energy difference between **1** and **3** (or **2** and **4**) is roughly governed by the difference between specific $\pi \rightarrow \pi^*$ excitations in **1** (or **2**) and $n_\sigma \rightarrow 3p_{zSi}$ excitations in **3** (or **4**) (in other words, we assume that correlation does not affect the energy differences **1**/**2** and **3**/**4**). This difference was computed at 7 kcal/mol for $H_2Si=CH_2/H\ddot{S}i\text{-}CH_3$ (see section III). Taking into account this correction, an estimate of the correlation corrected relative energies is given in Table IV leading to the ordering

$$\begin{array}{cccc} 2 < & 4 < & 1 < & 3 \\ 0 & 5 & 6 & 22\ \text{kcal/mol} \end{array}$$

This ordering will be discussed in section V.

The most interesting valence energy levels are reported in Table V. One can notice for **1** and **2** a raise of the highest π levels with respect to silaethylene (π = −8.54 eV) or to butadiene (π_1 = −12.09 eV; π_2 = −8.76 eV). The n_σ level in **4** is raised with respect to **3** or methylsilylene (η_σ = −8.61 eV). The $n_\sigma \rightarrow p_{\pi Si}$ (or HOMO–LUMO) gap is, however, comparable for **3** (9.37 eV), **4** (9.21 eV), and methylsilylene (9.36 eV). These gaps suggest that the singlet–triplet separation should be smaller in **4** than in **3** or methylsilylene. The 0.3-eV stabilization of the $\pi_{C=C}$ level in **4** with respect to ethylene (10.20 eV with the same basis set) illustrates the $\pi_{C=C} \rightarrow 3p_{zSi}$ conjugation.

Table V. Frontier Orbital Energies (in eV)

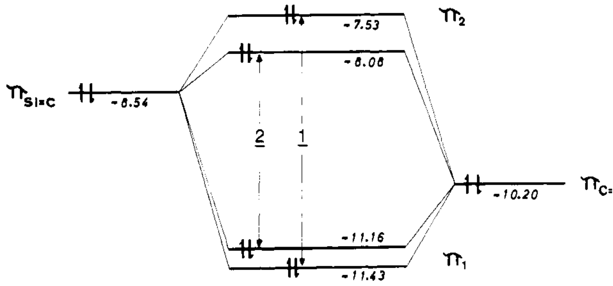
	1	2		3	4
4a″ (π_1^*)	+5.67	+4.78	4a″ ($\pi^*_{C=C}$)	+4.25	+4.51
3a″ (π_2^*)	+1.79	+2.20	3a″ ($p_{\pi Si}$)	+0.67	+1.01
2a″ (π_2)	−7.53	−8.08	9a′ ($n_{\sigma Si}$)	−8.70	−8.20
1a″ (π_1)	−11.43	−11.16	2a″ ($\pi_{C=C}$)	−9.83	−10.47

Table VI. d Atomic Populations on Silicon Atoms and Calculated Dipole Moments[a]

molecule	d_{Si}, e	μ, D
$SiH_2=CH_2$	0.17 (0.16)	0.81 (0.84)
$SiH_2=CHCH=CH_2$ (1)	0.16	1.18
$CH_2=SiHCH=CH_2$ (2)	0.20	2.05
$H\underset{..}{Si}CH_3$	0.11 (0.11)	1.04 (1.02)
$H\ddot{S}iCHCH=CH_2$ (3)	0.11	0.96
$\ddot{C}H_2\underset{..}{Si}CH=CH_2$ (4)	0.12	1.50

[a] DZ + d(Si and C) values in parentheses, DZ + d(Si) values otherwise.

Scheme I



C. Charge Distributions. The net atomic charges derived from Mulliken population analysis are reported for **1**, **2**, and silaethylene in Figure 7. With respect to silaethylene, the $^+Si=C^-$ polarity is diminished in **1** and enhanced in **2**, inducing in both cases a small dipole in the adjacent C=C bond. A somewhat strong reactivity of 2-silabutadiene (**2**) has been suggested[11] since the high polarity of the $C_1=Si$ bond can allow ionic attack, especially electrophilic attack on the highly negative C_1 site. The net atomic charge diagrams for **3**, **4** , and methylsilylene are reported in Figure 8. No great difference appears between methylsilylene and allylsilylene (**3**). In **4** the silicon atom (which is surrounded by two carbon atoms) is more positively charged, owing to σ effects. The resulting calculated dipole moments are reported in Table VI.

V. Discussion

A. Conjugation between a Si=C Bond and a C=C Bond. Relative Stabilities of 1 and 2. Starting from ethylenic localized π MO's for each of the Si=C or C=C fragment

$$\pi_{Si=C} = \alpha\chi_{Si} + \beta\chi_C \qquad (\alpha < \beta)$$

$$\pi_{C=C} = (1/\sqrt{2})(\chi_3 + \chi_4)$$

a zeroth-order interaction occurs between these occupied MO's, resulting in two separate occupied π MO's (π_1 and π_2) in both systems **1** and **2** (Scheme I). Since in $\pi_{Si=C}$ the largest amplitude is on the carbon atom, the off-diagonal Fock matrix element which is

$$\langle\pi_{Si=C}|F|\pi_{C=C}\rangle \simeq \beta\langle\chi_C|F|\chi_3\rangle \text{ in } \mathbf{1}$$

$$\langle\pi_{C=Si}|F|\pi_{C=C}\rangle \simeq \alpha\langle\chi_{Si}|F|\chi_3\rangle \text{ in } \mathbf{2}$$

will be larger in **1**, including for this compound a larger π_1–π_2 gap as can be verified in Table V and in Scheme I.

These interactions between occupied MO's have no influence on the total energy. The π contribution to the total energy may be divided in two parts: (i) the π polarization of the C=C bond by the $^+Si=C^-$ dipole which induces a small parallel dipole, and

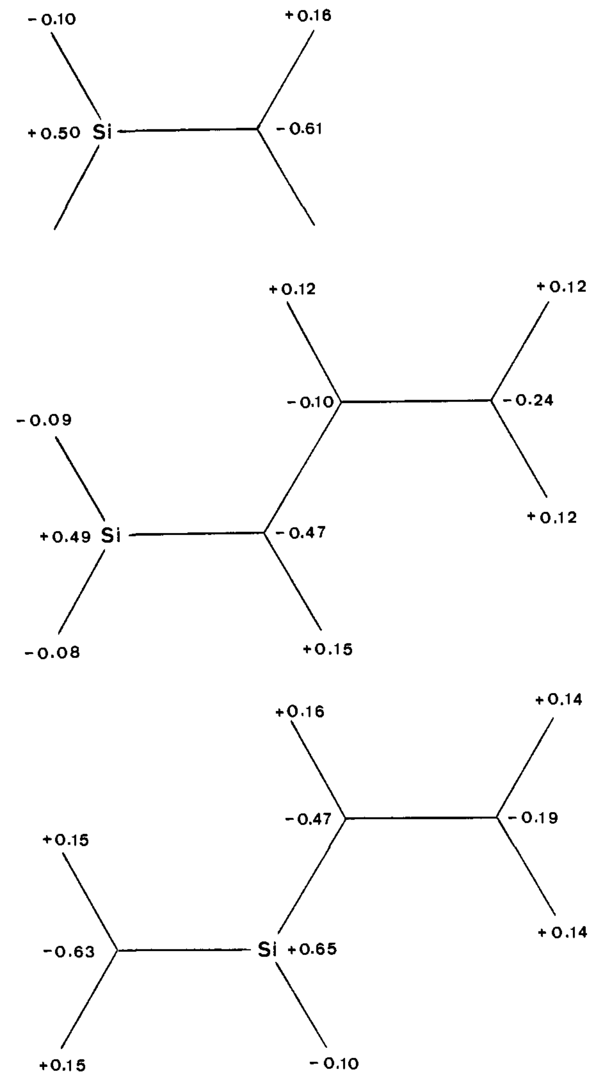
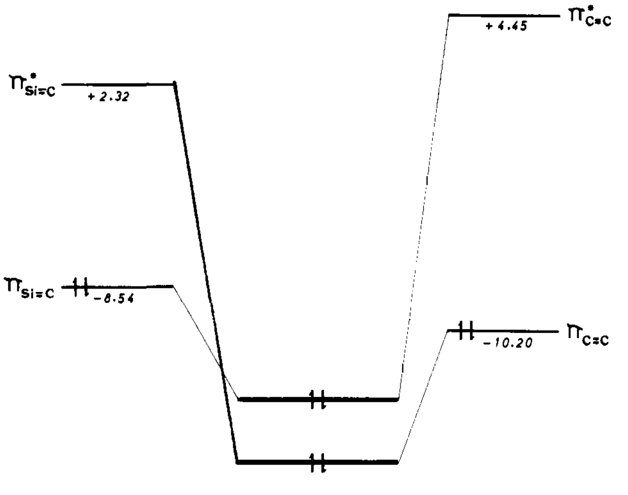


Figure 7. Net atomic charges on silaethylene, 1-silabutadiene (1), and 2-silabutadiene (2).

Scheme II



(ii) the π delocalization which allows the occupied π MO of one bond to take a component on the antibonding π^* MO of the other bond, according to Scheme II. Since in $\pi^*_{Si=C}$ the largest amplitude is on the silicon atom, the charge transfer in **1** will be smaller in the $\pi_{C=C} \rightarrow \pi^*_{Si=C}$ direction than in the $\pi_{Si=C} \rightarrow \pi^*_{C=C}$ direction, resulting in an overall π-electron transfer from the Si–C moiety toward the C–C moiety. For **2** the conclusions are reversed (the Möller–Plesset energy denominators are also smaller, $\Delta E_{\pi_{C=C}\rightarrow\pi^*_{Si=C}}$ (12.5 eV) < $\Delta E_{\pi_{Si=C}\rightarrow\pi^*_{C=C}}$ (13.0 eV)). Moreover, in the latter compound, another charge transfer is possible from $\pi_{C=C}$ to a vacant $d^*_{\pi Si}$ MO on silicon, which was not important in **1** where silicon is farther from χ_3.

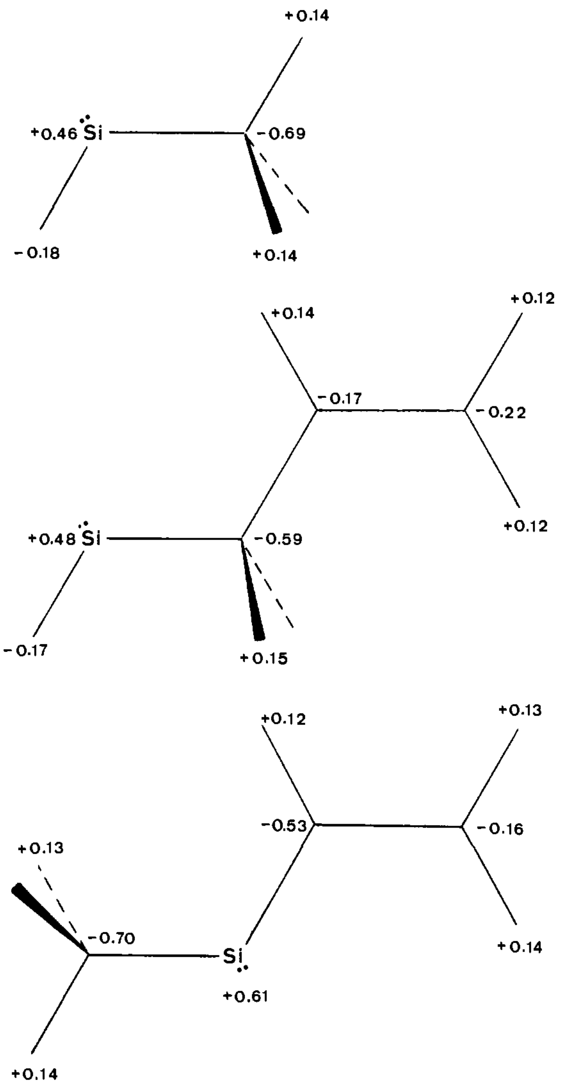


Figure 8. Net atomic charges on methylsilylene, allylsilylene (3), and methylvinylsilylene (4).

The calculated π distributions perfectly follow this qualitative interpretation,

$$\overset{+0.18}{\mathrm{Si}} = \overset{-0.18}{\mathrm{C}}$$

$$\overset{+0.16}{\mathrm{Si}} = \overset{-0.14}{\mathrm{C}} - \overset{+0.03}{\mathrm{C}} = \overset{-0.05}{\mathrm{C}}$$

$$\overset{-0.24}{\mathrm{C}} = \overset{+0.20}{\mathrm{Si}} - \overset{-0.03}{\mathrm{C}} = \overset{+0.07}{\mathrm{C}}$$

with an overall Si=C→C=C charge transfer in **1** (0.02 e) and a larger C=Si←C=C charge transfer in **2** (0.04 e). The role of d orbitals in 2-silabutadiene conjugation is confirmed by the population of d orbitals on the silicon atom; Table VI shows it remains low but significantly higher in **2** (0.20 e) than in **1** (0.16 e) or silaethylene (0.17 e). The overall π overlap populations (Figure 9a) confirm that the π conjugation on the central bond is always weak but larger in **2** than in **1** or in butadiene (40% of the important π Si–C_3 overlap population in **2** is due to p_π–d_π conjugation; see Figure 9b).

All these elements plead in favor of a larger π conjugation in **2** with respect to **1**, but they only concern the wave function. Simple ways to compute directly the delocalization (or resonance or conjugation) energies in conjugated hydrocarbons have been

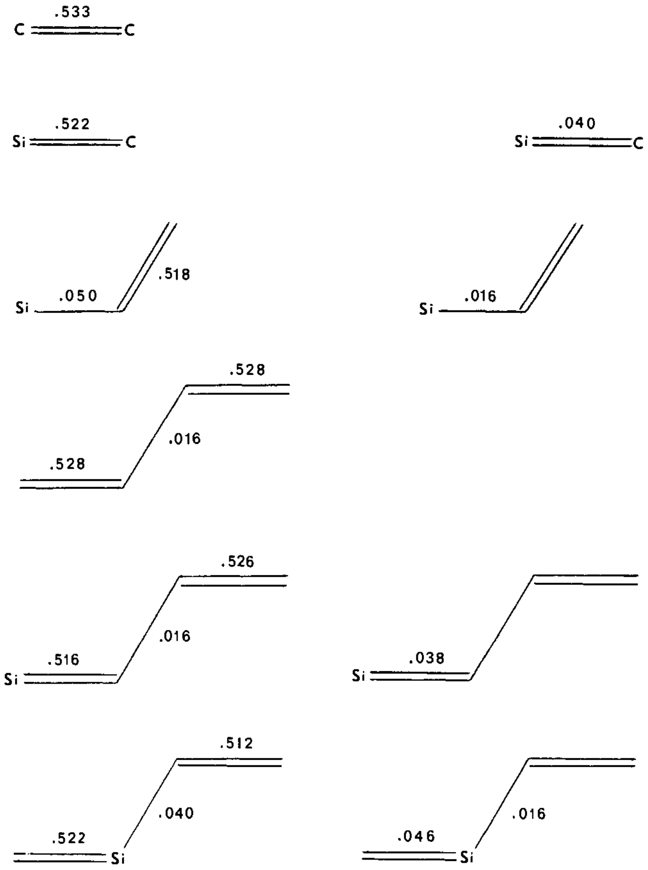


Figure 9. π-Overlap populations: (a) total π; (b) p_π–d_π.

proposed by Kollmar[24] and Daudey et al.[25] through a model wave function in which the SCF π orbitals are replaced by appropriate nonresonating localized π MO's in the field of the σ SCF distributions. Because of the strong polarity of σ and π frameworks in silabutadienes, the procedure of ref 25 cannot yield reliable results. Since neither the σ relaxation nor the relaxation of the polar π MO's is taken into account, the calculated resonance energies will be overestimated in silabutadienes. Indeed, this method[25] gave calculated vertical resonance energies of 10.3 kcal/mol for butadiene, which is quite reasonable, 13.7 kcal/mol for **1**, and 28.3 kcal/mol for **2**, which is certainly largely overestimated. This procedure appears therefore uncertain to measure the π conjugation in **1** and **2**. A less direct procedure uses the following bond separation reactions

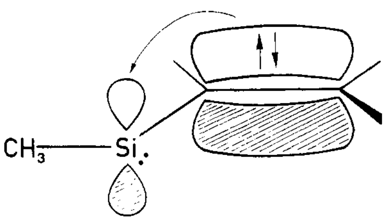
$$H_2Si{=}CH{-}CH{=}CH_2 + 2CH_4 \rightarrow H_2Si{=}CH_2 + H_3C{-}CH_3 + H_2C{=}CH_2 \quad (1)$$

$$H_2C{=}SiH{-}CH{=}CH_2 + CH_4 + SiH_4 \rightarrow H_2C{=}SiH_2 + H_3Si{-}CH_3 + H_2C{=}CH_2 \quad (2)$$

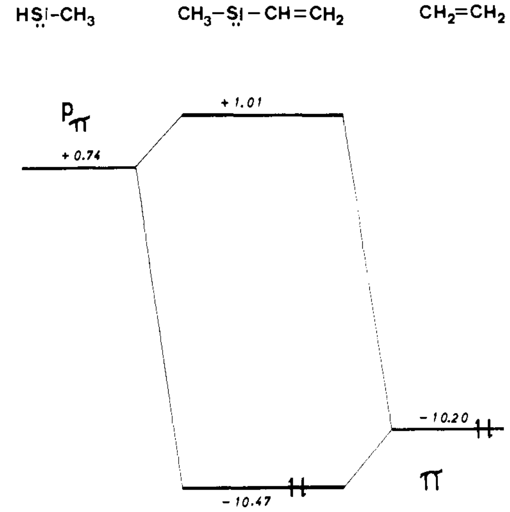
$$H_2C{=}CH{-}CH{=}CH_2 + 2CH_4 \rightarrow H_2C{=}CH_2 + H_3C{-}CH_3 + H_2C{=}CH_2 \quad (3)$$

The energies of these isodesmic reactions were computed at 5.7 kcal/mol for (1), 0.2 kcal/mol for (2), and 11.6 kcal/mol for (3), showing a weak conjugation energy for **2**. The use of rotational barriers as an estimate of the conjugation energy would support this conclusion.[26] However, the zero value for **2** does not seem meaningful and is in contradiction with the detailed analysis concerning the important π level shifts and charge migrations. One must remember that the bond separation method deals with overall σ and π changes (the Si_{sp^2}–C_{sp^2} single bond, for instance, is transformed into a Si_{sp^3}–C_{sp^3} single bond).

Scheme III



Scheme IV



One might invoke the well-known preference of silicon atom to be bound to carbon atom instead of hydrogen atom, as appears in the 1-silapropene vs. 2-silapropene energies calculated at the SCF level by Gordon:[6] $CH_3SiH{=}CH_2 < SiH_2{=}CHCH_3$ by 8.6 kcal/mol. This value relative to a methyl substitution can be regarded as an upper bound for the vinyl substitution relevant in our **1**/**2** comparison. As a conclusion, the 6-kcal/mol greater stability of 2-silabutadiene over 1-silabutadiene could result from both a larger π conjugation and a σ substitution preference.

B. Conjugation Stabilization of Si=C Bonds with Respect to the S̈i–C Silylene Forms. The 16-kcal/mol estimated stability of **1** over its silylene isomer **3** may be regarded as the result of two effects, namely, the 3.5-kcal/mol intrinsic stability of Si=C vs. S̈i–C (cf. section III) and the π-conjugation which would then be up to 12 kcal/mol. As concerns the **2**/**4** comparison, one may notice that conjugation also appears in the silylene **4** from the $\pi_{C=C}$ bond to the vacant $3p_z$ AO of the singlet silylene (Scheme III). Such a conjugation results in a 0.27-eV downward shift of the $\pi_{C=C}$ occupied MO (when compared to the ethylene value) and in an equal upward shift on the $p_{\pi Si}$ LUMO level (when compared to the methylsilylene value) (Scheme IV). Comparison of the following SCF relative energies

$$H\ddot{S}iCH_3 < H_2Si{=}CH_2 \qquad 1.5\ \text{kcal/mol}$$

$$CH_3\ddot{S}iCH{=}CH_2 < CH_2{=}SiHCH{=}CH_2 \qquad 2.1\ \text{kcal/mol}$$

suggests that π conjugation in **2** would be of the same magnitude, energetically, as the vinylsilylene-type delocalization in **4** since the σ frameworks are essentially the same in **2** and **4**. The 5-kcal/mol in favor of **4** should simply be attributed to the larger correlation energy in the Si=C bond.

C. Summary. This paper illustrates the competition and possible interference between two forms of unsaturations (double-bond formation and divalence) in silicon-containing molecules. Silaethylene is slightly more stable than methylsilylene; as expected, π-conjugation with a C=C bond appears to be an im-

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[24] Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

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[26] The rotational barrier around the central C–C bond in butadiene is sometimes taken as an index for the delocalization energy which occurs in the planar forms. This index has been criticized (ref 25) in view of the importance of hyperconjugation in perpendicular geometries. Actually the rotational barriers calculated in the rigid rotator model (6.5 kcal/mol for butadiene, 6.7 kcal/mol for **1** and 3.9 kcal/mol for **2**) are not sufficient to infirm the larger conjugation in **2** since they might result from a large $\pi_{C=C} \rightarrow d^*_{\pi Si}$ hyperconjugation in the latter compound.

J. Am. Chem. Soc. **1981**, *103*, 6319–6323

portant stabilizing factor for a Si═C bond. Analysis of monoelectronic energy shifts and charge migrations indicates this conjugation to be comparable with that occurring in butadiene, and suggests a somewhat larger interaction in **2** than in **1**; however, the use of bond separation isodesmic reactions does not confirm the π-conjugation to be responsible for the great stability of **2**. Conjugation strongly stabilizes 1-silabutadiene with respect to its silylene isomer, but in the case of 2-silabutadiene the π C═Si—C═C conjugation is balanced by the $\pi_{C═C} \rightarrow 3p_{zSi}$ π delocalization occurring in the silylene isomer.

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Multiconformational Synthetic Polypeptides

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Abstract: Polypeptides with two amino acid residues, one hydrophobic, L-leucine, the other hydrophilic, L-lysine, were synthesized by condensation of the dipeptide units Lys-Lys, Leu-Leu, Lys-Leu, and, in varying amounts, Leu-Lys. Their chains contained simultaneously sequences of alternatingly and randomly distributed Leu and Lys residues. The former sequences, if long enough, give rise in aqueous salted solutions to the formation of β structures and the latter to α helices, in such a way that for a given amount of each sequence, β, α, and eventually random coil, structures coexist in the same chain. These polypeptides undergo transconformations mimicking the self-organization of protein chains. Heating the samples increases the amount of β structure with loss of α helix. Increasing volumes of alcohols in aqueous solutions of alternating and random poly(Leu-Lys) induce an α helix. A β to α transition is also observed when the alcohol is added to an aqueous solution of alternating poly(Leu-Lys) previously transconformed in the β structure by addition of salt. Thus these simple multiconformational synthetic polypeptides may be useful as protein models for the study of chain folding in different environment.

It has been previously shown that polypeptides with alternating hydrophilic and hydrophobic residues take up systematically a β sheet structure in aqueous solution in the presence of salt. Poly(Glu-Ala) exhibits a circular dichroism spectrum typical of a β sheet structure after standing for several weeks in neutral aqueous solution[1]. Poly(Tyr-Glu) forms a soluble aggregate of antiparallel β chains below pH 10.5.[2] Seipke et al.[3] showed that alternating poly(Lys-Phe) adopts a β sheet structure in the presence of sodium perchlorate; so does poly(Tyr-Lys)[4] in the presence of NaCl. The β structure formation has been generalized to alternating polypeptides built up with leucyl or valyl residues combined to glutamyl or to lysyl residues.[5-7] For poly(Val-Lys), the existence of a specific bilayer with a hydrophobic interior and a hydrophilic exterior has been shown.[5] The corresponding random copolypeptides poly(Lys^{50},Phe^{50})[3] and poly(Leu^{50},Lys^{50})[8] exhibit an α helix under the same conditions. It was therefore thought that polypeptides containing both alternating and random sequences of hydrophilic and hydrophobic residues, i.e., lysyl and leucyl residues, may exhibit simultaneously β sheets and α-helical structures, modeling by the way the ordering of protein chains. Seven samples covering the range from random distribution to strict alternation of leucyl and lysyl residues were synthesized. The conformations of the polymers were studied by circular dichroism and infrared spectroscopy in aqueous solution of varying ionic strength, temperature, and hydrophobicity.

Statistical Analysis of the Sequences

The β fraction determined experimentally was compared with the fraction R_β of alternating leucyl and lysyl residues calculated by statistical analysis in a similar way as for alternating L and D residues,[9] supposing that no selection took place during the polymerization of the dipeptide monomers. For all $n \geq n_\beta$, where n is the number of consecutive alternating hydrophobic hydrophilic residues, and n_β is the minimum number of these residues required for a sequence to be included in a β-sheet structure,

$$R_\beta = (1 - 3\alpha)^{(n_\beta-1)/2}[1 + \alpha(3n_\beta - 7)/2 + 2\alpha^2(1 - n_\beta)] + \alpha^{(n_\beta+1)/2}[1 + 3n_\beta + 4\alpha(1 - n_\beta)]/2 \quad \text{(for odd } n_\beta\text{)}$$

and

$$R_\beta = (1 - 3\alpha)^{(n_\beta/2)-1}[1 + \alpha(3n_\beta - 10)/2 + 2\alpha^2(3 - 2n_\beta)] + \alpha^{n_\beta/2}(n_\beta + 4\alpha)/2 \quad \text{(for even } n_\beta\text{)}$$

(α is defined below)

These relations take into account the sequences formed by (Leu-Lys) and (Lys-Leu), eventually elongated by one amino acid residue at either extremity by adjunction of a (Lys-Lys) or (Leu-Leu) dipeptide monomer unit. For reasons explained elsewhere,[10] n_β was taken equal to 7 to draw the curve in Figure 2.

General Procedure for the Synthesis[11]

The samples were prepared by condensing *p*-nitrophenyl dipeptide esters according to the following scheme:

$$\left.\begin{array}{l}(\alpha)\ \text{HCl, H-Lys(Z)-Leu-ONp}\\(\alpha)\ \text{HCl, H-Leu-Leu-ONp}\\(\alpha)\ \text{HCl, H-Lys(Z)-Lys(Z)-ONp}\end{array}\right\} +$$

$$(1 - 3\alpha)\text{HCl, H-Leu-Lys(Z)-ONp} \xrightarrow[\text{DMF}]{\text{TEA}}$$

$$[\text{Leu-Lys(Z)}]_n \xrightarrow[\text{CHCl}_3]{\text{HBr}} (\text{Leu-Lys})_n$$

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[10] Brack, A.; Spach, G. *J. Mol. Evol.* **1979**, *13*, 35–46.

[11] The abbreviations employed follow the IUPAC–IUB recommendations (*J. Biol. Chem.* **1972**, *247*, 977) with, in addition, DCCI, dicyclohexylcarbodiimide; DCHA, dicyclohexylamine; TFA, trifluoroacetic acid; DCA, dichloroacetic acid; TEA, triethylamine; DMF, dimethylformamide.

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