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A Systematic Investigation on the Structure and Stability of the Lowest Singlet and Triplet States of Si_2H_4 and SiH_3SiH and the Analogous Carbon Compounds SiH_2CH_2, SiH_3CH, CH_3SiH, C_2H_4, and CH_3CH

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Abstract: SCF and electron correlation calculations are reported for the lowest singlet and triplet state of the title compounds. Geometry optimization and the determination of the complete harmonic force field has been performed within the Hartree–Fock method using flexible basis sets including d functions on the heavy atoms. Electron correlation energies were calculated by the CEPA-2 approach. The effect of electron correlation on CC, CSi, and SiSi bond distances and on the pertaining force constants is discussed. For fixed geometries large-scale CEPA calculations with 2d sets on the heavy atoms and one p set on the hydrogens were performed. Single–triplet splittings and relative stabilities of the various isomers were computed.

1. Introduction

Organosilicon compounds containing carbon–silicon or silicon–silicon double bonds are of great interest in experimental and theoretical chemistry. Because of the tendency of these compounds to form dimers or polymers, only few cases of stable monomers are known. Thus, most of the experimental evidence is rather indirect (for a review see ref 1). However, in recent years much progress has been made in the preparation and characterization of molecules containing silicon double bonds. For the first time a disilene structure, tetramesityldisilene, has been synthesized[2,3] and silaethene has been isolated in a matrix.[4] Also, a number of substituted silaethylenes have been reported (for references see, e.g., ref 4). On the other hand, the unsubstituted disilene has not been oserved so far.

Theoretical calculations on the Si_2H_4 and $SiCH_4$ systems have been performed by several groups[5–17] at various levels of sophistication ranging from SCF to CI treatments. Geometry optimization has been performed mostly on the double ζ SCF level, and the matrix of force constants has been determined only in very few cases. Little is known about the influence of polarization functions on calculated geometries in silicon-containing compounds.

This paper is a continuation of our SCF investigations on the Si_2H_4 system.[17] We want to present a systematic survey of the title molecules by using fairly flexible basis sets (including d functions) for geometry optimization and the determination of the complete harmonic force field at the SCF level. Thus, we are in the position to determine for all structures investigated within our method of calculation whether they are local minima or saddle points, etc., on the energy hypersurface. Correlation effects on the SiSi, SiC, and CC bond distances and force constants are discussed too. Moreover, for fixed geometries correlation energies were calculated employing extended basis sets (two d sets on the heavy atoms, one p set on hydrogen).

Even though our interest concentrates on the silicon-containing compounds, we treated the pure hydrocarbon systems ethylene and methylcarbene as well. For ethylene and its rearrangement to methylcarbene a number of SCF[18,19] and correlation energy calculations[20–25] exist. We think that our investigations will give also additional and, in some cases, more accurate information than was available before.

2. Computational Details

Closed-shell and open-shell restricted Hartree–Fock calculations have been performed with a program developed by Pitzer and co-workers[26,27] based on the HONDO integral subroutines.[28,29] The geometry optimizations were carried out using a modified HONDO gradient program.[30] Correlation energies were calculated by the CEPA-2 method[31] (for a

Chart I

	basis set no.	
C_2H_4	1	C: 8s4p1d (1.0) H: 3s
	2	C: 8s4p1d (1.0) H: 3s1p (0.65)
	3	C: 8s4p2d (0.4, 1.4) H: 3s1p (0.65)
$CSiH_4$	4	Si: 10s6p1d (0.4) C: 8s4p1d (1.0) H: 3s
	5	Si: 10s6p1d (0.4) C: 8s4p1d (1.0) H_C: 3s1p (0.65) H_{Si}: 3s1p (0.4)
	6	Si: 10s6p2d (0.2, 0.7) C: 8s4p2d (0.4, 1.4) H_C: 3s1p (0.65) H_{Si}: 3s1p (0.4)
Si_2H_4	7	Si: 10s6p1d (0.4) H: 3s
	8	Si: 10s6p1d (0.4) H: 3s1p (0.4)
	9	Si: 10s6p2d (0.2, 0.7) H: 3s1p (0.4)

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(1) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. *Acc. Chem. Res.* **1975**, *8*, 18.

(2) West, R.; Fink, M. J. *Science* **1981**, *214*, 1343.

(3) Masamune, S.; Hanzawa, Y.; Murakami, Sh.; Bally, Th.; Blount, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(4) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem.* **1981**, *93*, 615.

(5) Daudel, R.; Kari, R. E.; Poirier, R. A.; Goddard, J. D.; Csizmadia, I. G. *J. Mol. Struct.* **1978**, *50*, 115.

(6) Synder, L. C.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1979**, *101*, 5222.

(7) Roelandt, F. F.; van de Vondel, D. F.; van der Kelen, G. P. *J. Organomet. Chem.* **1979**, *165*, 151.

(8) Poirier, R. A.; Goddard, J. D. *Chem. Phys. Lett.* **1981**, *80*, 37.

(9) Blustin, P. H. *J. Organomet. Chem.* **1976**, *105*, 161.

(10) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9.

(11) (a) Strausz, O. P.; Robb, M. A. Theodorakopoulos, G.; Mezey, P. G.; Csizmadia, I. G. *Chem. Phys. Lett.* **1977**, *48*, 162. (b) Strausz, O. P.; Gosavi, R. K. Theodorakopoulos, G.; Csizmadia, I. G. *Ibid.* **1978**, *58*, 43. (c) Gosavi, R. K.; Gunning, H. E.; Strausz, O. P. *Ibid.* **1978**, *59*, 321.

(12) Schlegel, H. G.; Wolfe, S.; Mislow, K. J. *Chem. Soc., Chem. Commun.* **1975**, 246.

(13) Ahlrichs, R.; Heinzmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7452.

(14) (a) Goddard, J. D.; Yoshioka, Y.9; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 7644. (b) Yoshioka, Y.; Goddard, J. D.; Schaefer, H. F., III *Ibid.* **1981**, *103*, 2452. (c) Yoshioka, Y.; Schaefer, H. F., III *Ibid.* **1981**, *103*, 7366.

0002-7863/82/1504-5884$01.25/0

Table I. Total Energies (au) and Zero-Point Energies (kcal/mol) for the C_2H_4 System

	$-E$(SCF)[a]			$-E$(CEPA)[b]		
molecule and state	basis set 1	basis set 2	basis set 3	basis set 1	basis set 3	ϵ_0
ethylene						
^1A_g	78.02787	78.03404	78.03629	78.31841	78.37331	34.3
$^3A_2$	77.95290	77.96006	77.96080	78.21255	78.26716	29.5
methylmethylene						
$^1A'$	77.91649	77.92370	77.92746	78.19166	78.25298	33.0
$^3A''$	77.95248	77.95866	77.96009	78.20662	78.26188	34.6

[a] SCF geometry; see Figure 1. [b] Geometry: CEPA result for R_{CC}, SCF results for the other geometry parameters (see Figure 1).

Table II. Singlet-Triplet Splittings $\Delta E(T_1-S_0)$ for the Molecules Investigated[a]

	ΔE(SCF)			ΔE(CEPA)		
molecules	basis set 1	basis set 2	basis set 3	basis set 1	basis set 3	$\Delta H^0_{298.16}$
ethylene	47.1	46.4	47.4	66.4	66.6	62.8
methylmethylene	−22.6	−21.9	−20.5	−9.4	−5.6	−4.0
	basis set 4	basis set 5	basis set 6	basis set 4	basis set 6	
silaethylene	12.8	13.6	13.9	35.8	36.5	35.2
methylsilylene	10.4	10.4	9.9	22.9	24.7	25.3
silylmethylene	−37.2	−36.3	−34.1	−24.4	−20.3	−19.1
	basis set 7	basis set 8	basis set 9	basis set 7	basis set 9	
disilene	0.2	0.8	1.4	20.4	20.2	19.7
silylsilylene	3.5	2.5	2.3	15.0	15.8	16.5

[a] Energies are given in kcal/mol. A positive sign implies that the singlet state is more stable than the triplet state.

Table III. Relative Stabilities for Singlet and Triplet States[a]

	ΔE(SCF)			ΔE(CEPA)		
molecules and states	basis set 1	basis set 2	basis set 3	basis set 1	basis set 3	$\Delta H^0_{298.16}$
ethylene/methylmethylene						
S_0	−69.9	−69.2	−68.3	−79.6	−75.5	−74.2
T_1	−0.3	−0.9	−0.5	−3.7	−3.3	−7.4
	basis set 4	basis set 5	basis set 6	basis set 4	basis set 6	
silaethylene/methylsilylene						
S_0	8.6	4.9	2.7	3.6	−0.6	−3.2
T_1	11.0	8.1	6.7	16.5	11.1	6.6
silaethylene/silylmethylene						
S_0	−59.0	−55.8	−52.8	−76.6	−67.0	−65.5
T_1	−9.1	−5.9	−4.8	−16.4	−10.2	−11.2
	basis set 7	basis set 8	basis set 9	basis set 7	basis set 9	
disilene/silylsilylene						
S_0	8.0	7.2	5.6	−1.3	0.4	−0.1
T_1	4.7	5.4	4.7	4.1	4.8	3.1

[a] Energies are given in kcal/mol. A negative sign implies that the first structure in a given pair is more stable than the second one.

recent detailed formulation of the open-shell cases, see ref 32). We use a GUGA direct CI program as described in ref 33 which has been extended by us for the treatment of the CEPA equations. The virtual orbitals of the Fock operator are used for the construction of all singly and doubly substituted configurations. The valence-shell orbitals are correlated only.

The following Huzinaga basis sets[34] were used: carbon 8s4p contracted to (41111/211); silicon 10s6p (511111/3111); hydrogen 3s (21), scaling factor 1.44. One or two d sets for the carbon or silicon atoms, respectively, and one p set for hydrogen were added to give the final basis sets listed in Chart I (the exponents for the polarization sets are given in parentheses).

Geometry optimization and the calculation of the complete harmonic force field were performed at the SCF level with basis sets 1 and 4, respectively. The geometries for the Si_2H_4 system were taken from our previous investigation.[17] With basis sets 1, 4, and 7, respectively, CC, CSi, and SiSi bond distances were reoptimized at the CEPA level keeping the other geometry parameters constant. CEPA calculations with larger basis sets were done at the geometries obtained in this way. From our best energy differences (i.e., Δ E(CEPA) with the largest basis set), the

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(15) Rosmus, P.; Bock, H.; Solouki, B.; Maier, G.; Mihm, G. *Angew. Chem.* **1981**, *93*, 616.

(16) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1981**, *103*, 6313.

(17) Lischka, H.; Köhler, H.-J. *Chem. Phys. Lett.* **1982**, *85*, 467.

(18) (a) Pulay, P.; Meyer, W. *J. Mol. Spectrosc.* **1971**, *40*, 59. (b) Bock, Ch. W.; George, Ph.; Trachtman, M. *Ibid.* **1979**, *76*, 191.

(19) (a) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196. (b) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *Ibid.* **1975**, *97*, 5217. (c) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *Chem. Phys. Lett.* **1976**, *41*, 500.

(20) Nobes, R. H.; Radom, L.; Rodwell, W. R. *Chem. Phys. Lett.* **1980**, *74*, 269.

(21) (a) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P.v.R. *Chem. Phys. Lett.* **1982**, *85*, 145. (b) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469.

(22) Staemmler, V. *Theor. Chim. Acta* **1974**, *35*, 309.

(23) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys.* **1976**, *9*, 75.

(24) Brooks, B. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1979**, *101*, 307.

(25) Bonacic-Koutecky, V.; Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 5917.

(26) Pitzer, R. M. *J. Chem. Phys.* **1973**, *58*, 3111.

(27) Hsu, H.-L.; Davidson, E. R.; Pitzer, R. M. *J. Chem. Phys.* **1976**, *65*, 609.

(28) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111.

(29) King, H. F.; Dupuis, M. *J. Comput. Phys.* **1976**, *21*, 144.

(30) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998.

(31) (a) Meyer, W. *Int. J. Quantum Chem.* **1971**, *S5*, 341. (b) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017. (c) Meyer, W. *Theor. Chim. Acta* **1974**, *35*, 277.

(32) Staemmler, V.; Jaquet, R. *Theor. Chim. Acta* **1981**, *59*, 487.

(33) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. *Int. J. Quantum Chem., Symp.* **1981**, *15*, 91.

(34) Huzinaga, S., Approximate Atomic Functions I and II, University of Alberta, Canada, 1971.

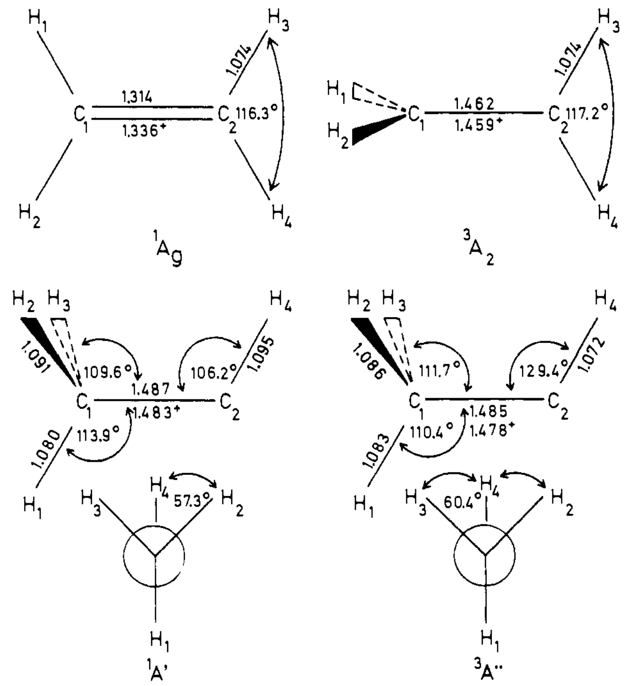

Figure 1. Geometries for the C_2H_4 system. An asterisk denotes the bond distances reoptimized at the CEPA level. Bond distances are given in angstroms, bond angles in degrees.

geometry parameters, and the vibrational frequencies, we obtain enthalpy differences at $T = 298.16$ K within the rigid rotator/harmonic oscillator approximation.[35]

3. Results and Discussion

3.1. Ethylene and Methylcarbene. Extensive CI calculations have been published by Buenker and Peyerimhoff[23] on the electronic ground and excited states of ethylene. Brooks and Schaefer[24] and Bonacic-Koutecky et al.[25] have treated the sudden polarization effect as a function of the pyramidalization of the CH_2 group in twisted ethylene. Experimental or partially optimized geometries have been employed. Completely optimized geometries and the matrix of harmonic force constants are available from the works of Pulay and Meyer[18a] and Bock et al.[18b] for the singlet ground state of ethylene. Singlet and triplet methylcarbene has been studied by Staemmler,[22] and several investigations on the conversion of methylcarbene to ethylene have been performed.[19-21,36] However, to our knowledge no extensive ab initio geometry optimization or harmonic force fields exist for triplet ethylene and triplet methylcarbene.

Geometries resulting from our calculations are shown in Figure 1. Total energies obtained with basis sets 1–3 are collected in Table I. The CC bond distance of 1.34 Å (CEPA value) in singlet ethylene agrees very well with the experimental one (1.339 Å[37]). R_{CC} for triplet ethylene is slightly smaller (1.46 Å) than the ones reported by Brooks and Schaefer[24] (1.49 Å) and by Buenker and Peyerimhoff[23] (1.48 Å).

Adiabatic singlet–triplet splittings and relative stabilities of ethylene vs. methylcarbene are listed in Tables II and III. Our value of 66.6 kcal/mol for $\Delta E(T_1-S_0)$ in ethylene is somewhat larger than the 62 kcal/mol obtained by Buenker and Peyerimhoff.[23] One has to note that the zero-point energy correction reduces ΔE by about 5 kcal/mol.

In the case of the singlet–triplet splitting in ethylene we also calculated ΔE values at the CI level and by means of the Davidson formula[38] using basis set 1. The respective energy differences are: ΔE(CEPA) = 66.4 kcal/mol, ΔE(CI) = 62.1 kcal/mol, and ΔE(Davidson) = 65.0 kcal/mol. One can see that the Davidson correction comes relatively close to the CEPA value. A similar situation is found for Si_2H_4 as well.

Table IV. Diagonal Quadratic Force Constants for the C_2H_4 System[a]

internal coordinates	ethylene ^1A_g this work	ethylene exptl[b]	ethylene $^3A_2$	methylmethylene $^1A'$	methylmethylene $^3A''$
stretch					
C_1C_2	11.2 9.56[c]	9.395	5.77 5.51[c]	4.89 4.73[c]	5.25 5.10[c]
C_1H_1	6.21	5.598	6.15	5.91	5.81
C_1H_2	6.21	5.598	6.15	5.56	5.69
C_2H_4	6.21	5.598	6.15	5.36	6.21
bend					
$H_1C_1C_2$	1.16	1.019	1.08	1.20	1.12
$H_2C_1C_2$	1.16	1.019	1.08	0.94	1.11
$H_4C_2C_1$	1.16	1.019	1.08	0.95	0.61
wag					
$H_1H_2C_1C_2$	0.310	0.259	0.001		
torsion					
$H_1C_1C_2H_4$				0.90	0.88
$H_2C_1C_2H_4$				0.79	0.86
$1/\sqrt{2}(H_1C_1C_2H_4 + H_2C_1C_2H_3)$	0.327	0.279	0.112		

[a] Stretching force constants are given in mdyn/Å, angular constants in mdyn Å. [b] Taken from ref 18b and 39. [c] CEPA value.

Table V. Harmonic Vibrational Frequencies (cm^{-1})[a,b]

	ethylene ^1A_g		ethylene twisted orthogonal $^3A_2$		methylmethylene $^1A'$		methylmethylene $^3A''$
a_{1g}	3307 (3152)	a_1	3300	a'	3279	a'	3368
	1842 (1655)		1627		3145		3252
	1493 (1370)		1176		3119		3183
a_{1u}	1149 (1044)	b_1	669		1611		1640
b_{1g}	3401 (3232)	b_2	3299		1553		1572
	1349 (1245)		1596		1358		1265
b_{1u}	1097 (969)	e	3388		1114		1131
b_{2g}	1112 (959)		1022		915		878
b_{2u}	3428 (3234)		70	a''	3198	a''	3236
	898 (843)				1978		2445
b_{3u}	3318 (3147)				1170		1239
	1630 (1473)				628		1002

[a] The experimental values[37] are given in parentheses. [b] The set of harmonic force constants obtained at the SCF level is used.

In our calculations methylmethylene has a triplet ground state ($\Delta E(T_1-S_0)$ = −5.6 kcal/mol) in accord with the findings of Staemmler.[22] On the other hand, Altmann et al.[19] find a splitting of only 0.3 kcal/mol in favor of the singlet state. We think that our result is more reliable because of the use of much larger basis sets and the explicit inclusion of electron correlation.

All the structures shown in Figure 1 are local minima on the energy hypersurface within our SCF calculations. Diagonal force constants and harmonic frequencies (derived from the complete SCF force field) are given in Tables IV and V. The CEPA CC stretching force constant for singlet ethylene agrees well with experiment.

Relatively large barriers have been reported by Altmann et al.[19] for the interconversion of singlet and triplet methylcarbene to singlet and triplet ethylene. A much smaller but still significant barrier (~40 kcal/mol) has been calculated by Harding[21b] for the triplet case. For the singlet case ab initio calculations by Nobes et al.[20] resulted in a very small barrier, and Raghavachari et al.[21] have shown that this barrier might not exist at all. Semiempirical calculations[34,38-40] give much smaller barriers as well. Good

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(35) Janz, G. J. "Thermodynamic Properties of Organic Compounds"; Academic Press: New York, 1967.

(36) Rayez-Meaume, M. T.; Decoret, C.; Dannenberg, J. J. *Chem. Phys. Lett.* **1978**, *55*, 431.

(37) Duncan, J. L.; Wright, I. J.; van Lerberghe, D. *J. Mol. Spectrosc.* **1972**, *42*, 463.

(38) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(39) Duncan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221.

(40) Bodor, N.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9103.

(41) Menêndez, V.; Figuera, J. M. *Chem. Phys. Lett.* **1973**, *18*, 426.

Table **VI.** Total Energies (au) and Zero-Point Energies (kcal/mol) for the $CSiH_4$ System

	$-E$(SCF)[a]			$-E$(CEPA)[b]		
molecule and state	basis set 4	basis set 5	basis set 6	basis set 4	basis set 6	ϵ_0
silaethylene						
$^1A_1$	328.92525	328.94024	328.95090	329.17465	329.25100	26.6
$^3A''$	328.90489	328.91859	328.92881	329.11760	329.19282	25.1
methylsilylene						
$^1A'$	328.93896	328.94809	328.95523	329.18035	329.24997	29.3
$^3A''$	328.92245	328.93155	328.93946	329.14393	329.21058	30.0
silylmethylene						
$^1A'$	328.83127	328.85141	328.86678	329.05262	329.14429	25.2
$^3A''$	328.89044	328.90927	328.92111	329.09148	329.17662	26.3

[a] SCF geometry; see Figure 2. [b] Geometry: CEPA result for R_{SiC}, SCF values for all other geometry parameters (see Figure 2).

Table VII. Diagonal Quadratic Force Constants for the $CSiH_4$ System[a]

	silaethylene		methylsilylene		silylmethylene	
internal coordinates	$^1A_1$	$^3A''$	$^1A'$	$^3A''$	$^1A'$	$^3A''$
stretch						
Si_1C_2	6.37	3.25	2.53	2.75	2.59	3.40
	5.13[b]	3.10[b]	2.45[b]	2.59[b]	2.43[b]	3.29[b]
H_1Si_1	3.05	2.87			3.03	3.00
H_2Si_1	3.05	2.87			2.90	2.94
H_4Si_2			2.49	2.90		
H_1C_1			5.87	5.86		
H_2C_1			5.66	5.83		
H_3C_2	6.23	6.10				
H_4C_2	6.23	6.20			5.65	6.35
bend						
$H_1Si_1C_2$	0.860	0.761			0.864	0.859
$H_2Si_1C_2$	0.860	0.761			1.12	0.841
$H_4Si_2C_1$			0.976	0.602		
$H_1Si_1H_2$		0.734				
$H_1C_1Si_2$			0.899	0.875		
$H_2C_1Si_2$			0.754	0.873		
$H_3C_2Si_1$	0.891	0.901				
$H_4C_2Si_1$	0.891	0.924			0.417	0.213
wag						
$H_1H_2Si_1C_2$	0.202					
$H_3H_4C_2Si_1$	0.213					
torsion						
$H_1Si_1C_2H_4$					0.709	0.720
$H_2Si_1C_2H_4$					0.692	0.700
$(1/\sqrt{2})(H_1Si_1C_2H_4 + H_2Si_1C_2H_3)$	0.198					
$(1/\sqrt{2})(H_1Si_1C_2H_3 + H_2Si_1C_2H_3)$		0.048				
$(1/\sqrt{2})(H_1Si_1C_2H_4 + H_2Si_1C_2H_4)$		0.029				
$H_1C_1Si_2H_4$			0.854	0.848		
$H_2C_1Si_2H_4$			0.819	0.844		

[a] Stretching force constants are given in mdyn/Å, angular constants in mdyn Å. [b] CEPA value.

Table **VIII.** Harmonic Vibrational Frequencies (cm^{-1})[a]

silaethylene			methylsilylene		silylmethylene	
$^1A_1$ SiH_2CH_2	SiD_2CH_2	$^3A''$	$^1A_1$	$^3A''$	$^1A'$	$^3A''$
a_1 3325	3338	a' 3390	a' 3275	a' 3278	a' 3209	a' 3411
2304	1660	a 3298	3171	3204	2296	2285
1558	1560	2234	2082	2250	2245	2266
1069	1057	1548	1551	1614	1029	1026
996	722	1001	1424	1431	922	1016
a_2 789	720	908	1009	959	899	799
b_1 909	897	761	672	689	672	740
564	436	633	637	601	545	544
b_2 3408	3421	a'' 2238	a'' 3235	a'' 3285	a'' 2252	a'' 2688
2308	1677	681	1645	1725	1779	2255
882	830	551	1174	1166	1073	753
498	407	313	660	792	710	646

[a] The set of harmonic force constants obtained at the SCF level is used.

agreement with the results of Raghavachari et al. is found for the stability difference between ethylene and methylcarbene. However, we find that staggered methylcarbene is a local minimum at the SCF level, whereas in the work of Raghavachari et al. this structure corresponds to a saddle point. The basis sets used are of comparable quality, but, nevertheless, energy differences are very small and this might explain the discrepancies.

3.2. Silaethylene, Methylsilylene, and Silylmethylene. Extended SCF and CI calculations have been carried out by several groups[13-16]. A complete calculation of the harmonic force field[12]

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(42) Gordon, M. S.; Saatzer, P. M.; Koob, R. D. *Chem. Phys. Lett.* **1976**, *37*, 127.

Table IX. Total Energies (au) and Zero-Point Energies (kcal/mol) for the Si_2H_4 System

molecule and state	$-E$(SCF)[a] basis set 7	basis set 8	basis set 9	$-E$(CEPA)[b] basis set 7	basis set 9	ϵ_0
disilene						
^{1}Ag	579.85314	579.87512	579.88957	580.05588	580.14338	20.3
^{3}B	579.85285	579.87384	579.88731	580.02332	580.11114	19.7
silylsilylene						
^{1}A'	579.86586	579.88652	579.89842	580.05382	580.14396	21.1
^{3}A"	579.86033	579.88247	579.89474	580.02985	580.11872	21.9

[a] SCF geometry; see ref 17. [b] Geometry: CEPA result for R_{SiSi} (see Table X), SCF values for all other geometry parameters (see ref 17).

and other calculations with smaller basis sets[9-11] exist in the literature.

Our results are shown in Figure 2 and in Tables II, III, and VI–VIII. We confirm the fact that singlet silaethylene is planar. The geometry parameters for all structures agree well with those in ref 13, 14, and 16. The SiC bond distance in singlet silaethylene is 1.71 Å, is close agreement with Trinquier and Malrieu[16] and Yoshioka et al.[14b] We thus support their conclusion that the SiC bond distance of 1.83 Å in $(CH_3)_2Si{=}CH_2$ obtained from electron diffraction experiments is too long. Similar to Goddard et al.[14a] and to Trinquier and Malrieu,[16] singlet silaethylene and singlet methylsilylene are found to be almost equally stable (see Table III). However, we note that zero-point-energy effects are quite significant in this case. A somewhat larger difference from the results of Goddard et al.[14a] is found for the triplet cases of silaethylene and methylsilylene. We obtain a ΔE(CEPA) of 11.1 kcal/mol compared with 18.7 kcal/mol of Goddard et al. $\Delta H^\circ_{298.16}$ is even reduced to 6.6 kcal/mol. Also for the singlet–triplet splitting of methylsilylene, some discrepancies occur when comparing with the value of Goddard et al. In most of the other cases agreement with the aforementioned authors is reasonably well. As can be seen from Tables II and III the addition of p functions to the hydrogen atoms and of a second d set to carbon and silicon does not exhibit dramatic effects. In some cases, on the other hand, these additional functions cannot be omitted when aiming for an accuracy of a few kcal/mol for energy differences.

All structures shown in Figure 2 are local minima within our SCF approach. However, as in the singlet case of CH_3CH the barrier of conversion from singlet SiH_3CH to singlet SiH_2CH_2 is found to be very small when electron correlation is taken into account.[14a] It might very well be that this barrier does not exist at all.

The diagonal force constants and the harmonic vibrations are shown in Tables VII and VIII. In the case of singlet silaethylene the spectrum for the deuterium isotope SiD_2CH_2 is given as well since it has been measured recently.[4] The antisymmetric and symmetric SiH and SiD stretching vibrations have been used for identification of the silaethylene structure. The following corresponding frequencies were measured:[4] SiH_2CH_2, 2239 and 2219 cm^{-1}; SiD_2CH_2, 1635 and 1600 cm^{-1}. The results obtained by us are (see also Table VIII): SiH_2CH_2, 2308 and 2304 cm^{-1}; SiD_2CH_2, 1677 and 1660 cm^{-1}. Our results are lower by ~170 cm^{-1} than the ones published by Schlegel et al.[12] and are still somewhat higher than the experimental data. However, the latter fact is reasonable because of the systematic errors of the Hartree–Fock approximation which we have used for the computation of force constants. The calculated shift of the frequencies when going from SiH_2CH_2 to SiD_2CH_2 agrees nicely with the observed one. Therefore, our findings support the experimental assignments. The SiH stretching vibration in the CSi single bonded system CH_3SiH is 2082 cm^{-1} and thus significantly lower than the SiH stretching vibration in silaethylene.

3.3. Disilene and Silylsilylene. Our SCF results on the Si_2H_4 system can be found in ref 17. The main progress with respect to the previous work of Poirier and Goddard[8] was the determination of the true minimum structure of triplet disilene as a twisted bent form. The correlation energy calculations presented in this work (see Table IX) also deviate to a large extent from their results. We find singlet disilene and silylsilylene almost equally stable (Table III), whereas Poirier and Goddard report stability differences between 8 and 10 kcal/mol. Similar discrepancies exist in other cases too.

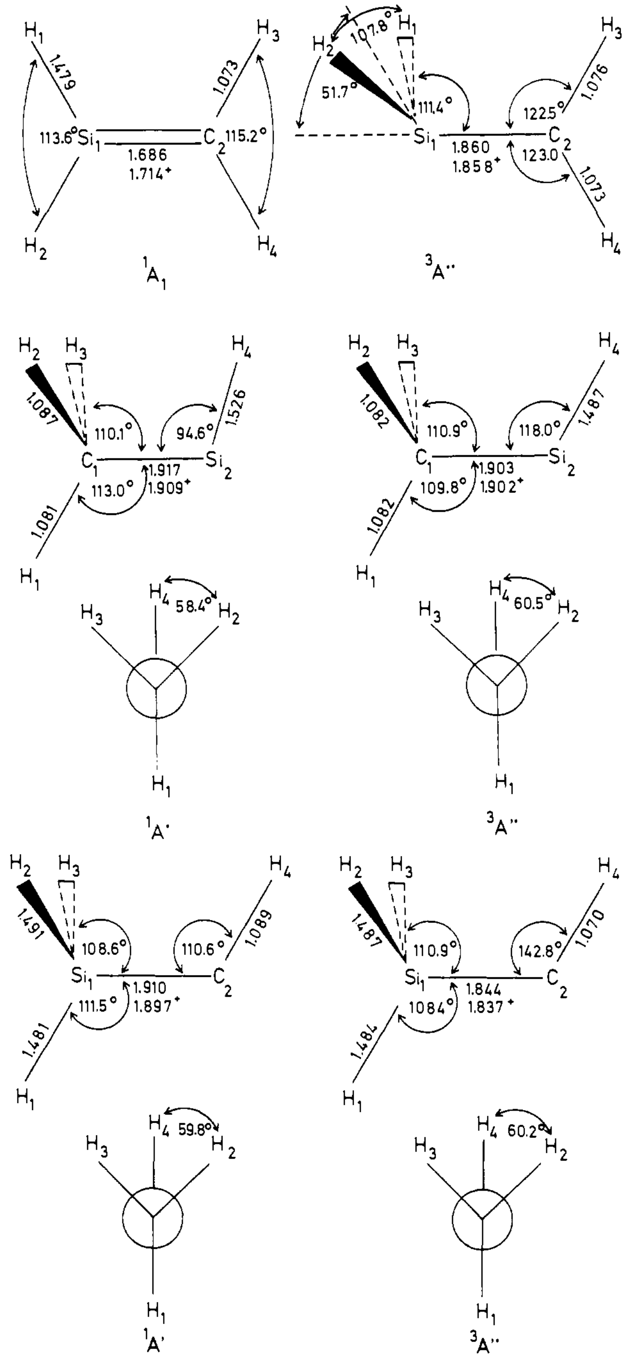

Figure 2. Geometries for the $CSiH_4$ system. An asterisk denotes the bond distances reoptimized at the CEPA level. Bond distances are given in angstroms, bond angles in degrees.

The SiSi bond distance and the SiSi stretching force constant were determined at the CEPA level. The results are collected

Table X. Electron Correlation Effects on the Si-Si Bond Distance and Stretching Force Constant in the Si_2H_4 System

	R_{SiSi} (Å)		K_{SiSi} (mdyn/Å)	
	SCF	CEPA	SCF	CEPA
disilene				
^1Ag	2.127	2.171	3.50	2.28
^3B	2.407	2.378	1.53	1.51
silylsilylene				
$^1A'$	2.479	2.453	1.30	1.24
$^3A''$	2.395	2.374	1.57	1.51

in Table X. As expected, in singlet disilene the bond distance is increased and the force constant is decreased by inclusion of electron correlation effects. In the other cases, in which Si-Si single bonds are involved, a reduction of the SiSi bond distance is observed. In the pair-energy approach one can visualize the situation in the following way: for singlet disilene the intrapair contributions of the Si-Si σ and π bonds increase in absolute value upon stretching the SiSi bond. This leads to the well-known increase of the equilibrium bond distance when compared to the SCF value. For the single bonded systems the just-mentioned effect is not so important. An additional, opposing factor becomes relevant, namely, the decrease (in absolute value) of interpair energies which leads to a reduction of the equilibrium distance. A similar, but not so pronounced effect can be found in the carbon-containing systems as well (see Figurs 1 and 2).

4. Summary

Geometries, harmonic force fields, and stability differences have been derived in a systematic and consistent way for the title molecules. One question of great chemical interest is the double-bond character of the SiSi bond in disilene. We do not attempt to give an elaborate discussion on that problem but simply want to look at a few properties of the energy surface and make a comparison with the corresponding quantities for ethylene and silaethylene.

The SiSi bond length in singlet disilene is considerably shorter than that in purely single-bonded compounds like silylsilylene. The effects are comparable with those for C_2H_4 and SiH_2CH_2. The SiSi force constant in disilene is larger than in silylsilylene. These two factors demonstrate the double-bond character of the SiSi bond in disilene. On the other hand, disilene is not so rigid as ethylene or silaethylene. In fact, it has been shown in ref 8 and 17 that the equilibrium structure of disilene is not completely planar or at least that the potential curve for the out-of-plane motion of the SiH_2 groups is very flat in the region of the energy minimum.

From a practical point of view it is interesting to note that the geometries obtained from basis sets including d functions (especially on silicon) do not deviate substantially from those calculated without d functions. However, these findings should be considered with caution. There is, of course, no guarantee that for other, even similar systems the same situation will hold.

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Registry No. Si_2H_4, 15435-77-5; SiH_3SiH, 50420-90-1; SiH_2CH_2, 51067-84-6; SiH_3CH, 66605-30-9; CH_3SiH_2, 24669-75-8; $H_2C{=}CH_2$, 74-85-1; CH_3CH, 4218-50-2.

Electronic Structure of Long Polyiodide Chains

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Abstract: The electronic structure of periodic one-dimensional polyiodides is studied for both $(I_3^-)_\infty$ and $(I_5^-)_\infty$ systems. The deformation from the equidistant arrangement toward the $(I_3^-)_\infty$ structure, as well as from the linear toward zigzag chains, permits a rationalization of the experimentally found structures. The role of electron delocalization in their compounds with high electrical conductivity is examined.

Short contacts of the I_3^- or I_5^- polyiodide ions aggregated together in several complex materials of channel inclusion compounds[1-22] indicate electron delocalization[8,15,19-21] along these long polyiodide (PI) chains. The crystal structure data of these materials indicate different degrees of delocalization. It has been repeatedly suggested[5,8,15,19,21] that electronic conduction may take

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(1) (a) R. E. Rundle, J. F. Foster, and R. R. Baldwin, *J. Am. Chem. Soc.*, **66**, 2116 (1944); (b) C. D. West, *J. Chem. Phys.*, **15**, 689 (1947).

(2) (a) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951); (b) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).

(3) F. Cramer, *Recl. Trav. Chim. Pays-Bas* **75**, 891 (1956).

(4) J. M. Reddy, K. Knox, and M. B. *Robin, J. Chem. Phys.*, **40**, 1082 (1964).

(5) (a) K. Huml, *Acta Crystallogr.*, **22**, 29 (1967); (b) V. Hadek, *J. Chem. Phys.*, **49**, 5202 (1968); (c) V. Hadek, P. Zach, K. Ulbert, and J. Honzl, *Collect. Czech. Chem. Commun.*, **34**, 3139 (1969).

(6) A. Gleizes, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 3545 (1975).

(7) H. Endres, H. J. Keller, M. H.-Belombe, W. Moroni, H. Pritzkow, and J. Weiss, *Acta Crystallogr., Sect. A*, **32**, 954 (1976).

(8) (a) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961); (b) R. Bersohn and C. Isenberg, *ibid.*, **35**, 1640 (1961).

(9) a) L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, C. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, and I. F. Shchegolev, *J. Chem. Soc., Chem. Commun.*, 720 (1976); (b) D. L. Smith and H. R. Luss, *Acta Crystallogr., Sect. B*, **33**, 1744 (1977); (c) R. B. Samoano, S. P. S. Yen, V. Hadek, S. K. Khanna, M. Novotny, T. Datta, A. M. Hermann, and J. A. Woollam, *Phys. Rev. B*, **17**, 2853 (1978).

(10) H. V. Düker, B. Freckmann, H. Niebuhr, M. Plewa, and K. F. Tebbe, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **149**, 120 (1979).

(11) (a) B. Hilti and C. W. Mayer, *Helv. Chim. Acta*, **61**, 501 (1978); (b) G. Rihs, Ciba-Geigy Internal Communication 1978.

(12) (a) H. Strzelecka, C. Weyl, and J. Rivory, *Lect. Notes Phys.* **96**, 348 (1979); (b) S. Flandrois, C. Coulon, J. Amiell, P. Delhaes, and P. Dupnis, *ibid.*, **96**, 188 (1979); (c) D. Chasseau, A. Filhol, J. Gautier, C. Hauw, and W. Steiger, *Chem. Scr.*, **17**, 97 (1981).

(13) (a) F. H. Herbstein and M. Kapon, *Nature (London), Phys. Sci.*, **239**, 153 (1972). (b) J. A. Kramer, F. H. Herbstein, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **102**, 2293 (1980).

(14) F. H. Herbstein and M. Kapon, *Acta Crystallogr., Sect. A*, **28**, S74 (1972).

(15) M. Noltenmeyer and W. Saenger, *Nature (London)*, **259**, 629 (1976).

(16) F. Cramer, U. Bergmann, P. C. Manor, M. Noltenmayer, and W. Saenger, *Justus Liebigs Ann. Chem.*, 1169 (1976).

(17) (a) M. Noltenmeyer and W. Saenger, *J. Am. Chem. Soc.*, **102**, 2710 (1980); (b) R. C. Teitelbaum, S. L. Reeby, and T. J. Marks, *ibid.*, **102**, 3322 (1980).

(18) H. Endres and J. P. Pouget, *Chem. Scr.*, **17**, 137 (1981).

(19) J. H. Perlstein, *Angew. Chem.*, **89**, 534 (1977).

(20) M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **32**, 161 (1976).

0002-7863/82/1504-5889$01.25/0