anion corresponding to proton loss from dimethylsilylene has been attributed to significant negative charge delocalization to silicon. Attempts to measure the acidity of dimethylsilylene have met with marginal success and suggest that its acidity is close to that of MeOH.

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Registry No. 1, 10124-62-6; 2, 6376-86-9; N_2O, 10024-97-2; CO_2, 124-38-9; CS_2, 75-15-0; COS, 463-58-1; NH_2^-, 17655-31-1; F^-, 16984-48-8.

π-Bond Strengths in Main-Group Olefin Analogues

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π-Bond strengths in main-group olefin analogues $H_2X{=}CH_2$ (X = C, Si, Ge, Sn) have been obtained theoretically from direct energy differences between planar (π-bonded) and perpendicular (biradical) structures and, according to a procedure proposed by Benson, from the energies of disproportionation of the products of hydrogen atom addition. Both methods yield nearly the same π-bond strengths: C=C, 64–68 kcal mol^{-1}; C=Si, 35–36 kcal mol^{-1}; C=Ge, 31 kcal mol^{-1}; C=Sn, 19 kcal mol^{-1}. The similarity of π-bond energies for silaethylene and germaethylene is rationalized in terms of d-block contraction.

Introduction

Very few compounds exist which incorporate multiple bonds between carbon and its heavier main-group analogues. In fact, only for silicon have stable, isolable compounds with double bonds to carbon been prepared. Among the simplest of these are 1,1-dimethylsilaethylene and parent silaethylene, both of which have now been detected in the gas phase.[1-3] An electron diffraction study of the former[3] has suggested a silicon–carbon double-bond length of 1.83 Å, not markedly shorter than typical single linkages, e.g., 1.875 Å in tetramethylsilane.[4] Significantly shorter bond distances have, however, been reported from X-ray crystal structures of $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl) (Si=C = 1.764 Å)[5] and both a tetrahydrofuran adduct of $Me_2Si{=}C(SiMe_3)[Si(Me)(t\text{-}Bu)_2]$ (Si=C = 1.747 Å)[6a] as well as the corresponding tetrahydrofuran-free complex (Si=C = 1.702 Å).[6b] These data, together with the results of high-level quantum chemical calculations[7,8b,c] which suggest Si=C bond lengths in the vicinity of 1.70 Å in simple silaolefins, cast doubt on the validity of the bond distance obtained in the electron diffraction work.

A number of experimental and theoretical estimates of π-bond energies for compounds incorporating double bonds between carbon and silicon have appeared in the literature.[7e,8] These estimates, for the most part based on comparisons with hypothetical singlet biradicals, i.e., incorporating twisted double bonds, are in the range of 34–46 kcal mol^{-1} and are to be compared with an experimentally determined π-bond strength of 65 kcal mol^{-1} in ethylene (obtained from the rate of cis–trans isomerization in 1,2-dideuterioethylene[9]). The highest level theoretical work[7e] is in accord and suggests an energy difference of 37 kcal mol^{-1} between planar silaethylene and a twisted singlet biradical. Very little experimental data exist for compounds incorporating double bonds between carbon and its main-group analogues beyond silicon. Pietro and Hehre[8d] have estimated π-bond strengths of 43, 45, and 30 kcal mol^{-1} in 1,1-dimethylgermaethylene, 1,1-dimethylstannaethylene, and 1,1-dimethylplumbaethylene, respectively, on the basis of gas-phase deprotonation thresholds for trimethylgermyl, trimethylstannyl, and trimethylplumbyl cations. These authors have noted, however, that the values for the germanium and tin systems appear to be out of line with the π-bond strengths in silicon compounds and have cautioned about their dependence on ancillary experimental thermochemical data of uncertain quality. The only previous theoretical estimate for the π-bond strength in germaethylene, 29 kcal mol^{-1} from a pseudopotential SCF method,[10] is, as might

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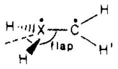
Table I. Equilibrium Geometries for Planar and Twisted Forms of Ethylene (UHF/3-21G) and Its Main-Group Analogues (UHF/3-21G$^{(*)}$)[a]

		X			
molecule	geometrical parameter	C	Si	Ge	Sn
$H_2X{=}CH_2$	r_{XC}	1.315	1.691	1.773	1.982
	r_{XH}	1.074	1.467	1.536	1.734
	r_{CH}	1.074	1.076	1.074	1.074
	∠HXH	116.2	114.0	114.0	112.1
	∠HCH	116.2	114.8	116.5	116.2
$H_2X^{\bullet}{-}CH_2^{\bullet}$[b]	r_{XC}	1.469	1.858	1.956	2.167
	r_{XH}	1.077	1.478	1.552	1.753
	r_{CH}	1.077	1.077	1.076	1.078
	$r_{CH'}$	1.077	1.080	1.078	1.079
	flap	180.0	130.4	129.0	125.8
	∠HXH	117.4	109.2	109.8	108.8
	∠HCX	121.3	122.6	121.6	121.8
	∠H′CX	121.3	122.5	122.0	122.8

[a] Bond lengths in angstroms and bond angles in degrees. [b] Geometrical parameters refer to



be expected, smaller than the bond energy in silaethylene. No nonempirical molecular orbital calculations appear to have previously been reported for molecules incorporating a tin–carbon double bond. A MNDO study of dimethylstannaethylene[11] shows a tin–carbon double-bond length which is 0.13 Å shorter than the analogous single-bond distances calculated for the molecule, suggestive of π bonding. The same calculations also show that the corresponding perpendicular triplet biradical is of nearly equal stability, compared with a singlet–triplet energy splitting of almost 100 kcal mol^{-1} in ethylene.[12] The authors interpret this latter result as evidence of only a very weak π bond (if any at all) in the species.[11]

While the primary goal of this paper is to assign π-bond strengths in the series of simple main-group olefin analogues $H_2X{=}CH_2$ (X = C, Si, Ge, Sn) on the basis of a uniform level of nonempirical molecular orbital theory, a second major objective is to establish an alternative criterion by which π-bond strengths may be assessed. That is to say, the usual measure, comparison of energies for planar and twisted double-bond configurations, may not be ideal or be applicable in all cases. For example, it has previously been noted that the low interconversion barriers measured[13] and calculated[14] for π bonds between carbon and left-hand transition metals probably do not accurately portray their strength. Furthermore, the definition of π-bond strength in terms of rotational barrier is obviously not applicable to the description of the strength of triple bonds or of double bonds involving terminal atoms, e.g., CO linkages in carbonyl compounds.

An alternative definition, originally proposed by Benson,[15] relates π-bond strength to the difference in energies of hydrogen atom addition to the unsaturated compound and to the resulting free radical, e.g., in ethylene

$$E_\pi = \Delta E(H_2C{=}CH_2 + H^{\bullet} \rightarrow H_3C{-}CH_2^{\bullet}) - \Delta E(H_3C{-}CH_2^{\bullet} + H^{\bullet} \rightarrow H_3C{-}CH_3)$$

Table II. Equilibrium Geometries for Planar and Twisted Forms of Ethylene and Silaethylene (UHF/6-31G*)[a]

		X	
molecule	geometrical parameter	C	Si
$H_2X{=}CH_2$	r_{XC}	1.317	1.694
	r_{XH}	1.076	1.467
	r_{CH}	1.076	1.076
	∠HXH	116.2	114.2
	∠HCH	116.2	115.0
$H_2X^{\bullet}{-}CH_2^{\bullet}$[b]	r_{XC}	1.465	1.863
	r_{XH}	1.078	1.479
	r_{CH}	1.078	1.077
	$r_{CH'}$	1.078	1.080
	flap	180.0	130.4
	∠HXH	117.0	109.2
	∠HCX	121.5	122.7
	∠H′CX	121.5	122.6

[a] Bond lengths in angstroms and bond angles in degrees. [b] See footnote *b* of Table I for description of geometrical parameters.

In effect, the fact that (in this case) the (methyl) CH bond energy in ethyl radical is much smaller than that in ethane is attributed entirely to the rupture of the CC π bond. The Benson analysis is also applicable to the olefin analogues dealt with in this paper. In this case, addition of hydrogen needs to be to the same atom in both steps, i.e.

$$E_\pi = \Delta E(H_2X{=}CH_2 + H^{\bullet} \rightarrow H_3X{-}CH_2^{\bullet}) - \Delta E(H_2X^{\bullet}{-}CH_3 + H^{\bullet} \rightarrow H_3X{-}CH_3)$$

$$E_\pi = \Delta E(H_2X{=}CH_2 + H^{\bullet} \rightarrow H_2X^{\bullet}{-}CH_3) - \Delta E(H_3X{-}CH_2^{\bullet} + H^{\bullet} \rightarrow H_3X{-}CH_3)$$

Theoretical Methods

All structures have been obtained by using the 3-21G$^{(*)}$ (3-21G for carbon and hydrogen) basis sets, recently extended through third- and fourth-row, main-group elements.[16] In addition, optimizations on molecules containing first- and second-row elements only have been performed by using the 6-31G* polarization basis sets,[17] both at the unrestricted Hartree–Fock (UHF) and second-order unrestricted Møller–Plesset (UMP2)[18] levels.

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Table III. Total Energies (hartrees)

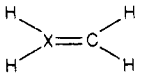
molecule	X	UHF/3-21G$^{(*)}$// UHF/3-21G$^{(*)a}$	UHF/6-31G*// UHF/6-31G*	UMP2/3-21G$^{(*)}$// UHF/3-21G$^{(*)b}$	UMP2/6-31G*// UHF/6-31G*
$H_2X{=}CH_2$	C	−77.600 99	−78.031 72	−77.780 15	−78.284 36
	Si	−327.392 11	−329.037 26	−327.566 47	−329.249 98
	Ge	−2105.419 99		−2105.616 99	
	Sn	−6036.630 58		−6036.816 82	
$H_2X^{\bullet}{-}CH_2^{\bullet}$	C	−77.537 10	−77.968 62	−77.677 53	−78.178 35
	Si	−327.375 65	−329.022 61	−327.510 71	−329.193 08
	Ge	−2105.413 04		−2105.567 18	
	Sn	−6036.646 28		−6036.786 19	
$H_2X^{\bullet}{-}CH_3$	C	−78.163 64	−78.597 14	−78.327 80	−78.835 38
	Si	−328.002 80	−329.651 82	−328.161 85	−329.851 17
	Ge	−2106.042 74		−2106.221 68	
	Sn	−6037.275 76		−6037.440 56	
$H_3X{-}CH_2^{\bullet}$	C	−78.163 64	−78.597 14	−78.327 80	−78.835 38
	Si	−327.996 06	−329.643 74	−328.144 71	−329.827 64
	Ge	−2106.021 62		−2106.190 24	
	Sn	−6037.241 34		−6037.393 88	
$H_3X{-}CH_3$	C	−78.793 95	−79.228 75	−78.981 59	−79.494 56
	Si	−328.622 74	−330.272 35	−328.795 25	−330.485 01
	Ge	−2106.650 50		−2106.843 72	
	Sn	−6037.869 80		−6038.047 27	

[a] UHF/3-21G//UHF/3-21G for X = C. [b] UMP2/3-21G//UHF/3-21G for X = C.

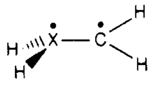
Comparison of these data with those obtained by using the smaller 3-21G$^{(*)}$ (3-21G) representations serves to calibrate the latter. The GAUSSIAN 85 series of computer programs has been employed throughout.[19]

Results and Discussion

As commented in the Introduction, the π-bond strength in ethylene has usually been related to the experimentally determined energy of cis–trans isomerization of dideuterioethylene.[9] More generally, bond strengths in olefin analogues may be given by the difference in stabilities between planar systems **1** and twisted singlet biradicals **2**.



1



2

Calculated (UHF/3-21G$^{(*)}$[20]) equilibrium structures for **1** and **2** for X = C, Si, Ge, and Sn are provided in Table I. UHF/6-31G* structural data for the carbon and silicon systems are provided in Table II. Total energies for these and other systems discussed in this paper both at UHF and UMP2 levels are given in Table III. All planar forms **1** have been established to be local minima by way of normal-mode analyses (on the UHF/3-21G$^{(*)}$ energy surfaces only); biradical structures **2** have been confirmed as first-order saddle points, i.e., characterized by a single imaginary frequency.

Note that some geometrical parameters (aside from XC bond lengths) differ significantly between structure types **1** and **2**. In particular, note the puckering about heteroatom center in all biradicals **2** (except dimethylene). These structural differences call into question the strict definition of π-bond strength in terms of rotational barrier.

Bond lengths in planar forms **1** are generally in good agreement with previous theoretical calculations. Specifically, the calculated silicon–carbon lengths in silaethylene, 1.691 Å at 3-21G$^{(*)}$ and 1.694 Å at 6-31G*, closely match the range of previously reported theoretical values (1.686–1.722 Å[7,8b,c]). Similarly, the 3-21G$^{(*)}$ value for the length of the Ge=C double bond, 1.773 Å, is in line with previous theoretical determinations, which range from 1.752 to 1.776 Å.[10,21] While no nonempirical molecular orbital calculations appear to have previously been reported for molecules containing a tin–carbon multiple bond, the results of an MNDO study on dimethylstannaethylene[11] show an Sn=C bond length of 1.92 Å. The present calculations suggest a somewhat greater bond length, 1.982 Å, although one which is shorter than typical for a SnC single linkage, e.g., 2.144 Å in $Sn(CH_3)_4$ from electron diffraction work,[4] by about the same amount (0.16 Å) as typical differences in double- and single-bond lengths in analogous silicon (0.16 Å) and germanium (0.17 Å) systems.

Note that all calculated Si=C bond lengths in silaethylene are significantly shorter than those reported in the crystal structures of $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), 1.764 Å,[5] and $Me_2Si{=}C(SiMe_3)[Si(Me)(t\text{-}Bu)_2]$/tetrahydrofuran, 1.747 Å.[6a] On the other hand, the observed Si=C distance in $Me_2Si{=}C(SiMe_3)[Si(Me)(t\text{-}Bu)_2]$,[6b] 1.702 Å, is in much better accord with the range of calculated values. Previous experience[22] suggests that the best of the Hartree–Fock methods applied here (UHF/6-31G*) provides a good overall account of equilibrium structure, generally underestimating bond lengths by 0.01–0.02 Å, while simple correlation methods such as UMP2/6-31G* (which yields a silicon–carbon distance in silaethylene of 1.715 Å) generally overestimates bond lengths by 0.01–0.02 Å. Discrepancies between calculated and experimental bond lengths in these systems have already been noted by Apeloig and Karni,[7d] who have suggested that substituent effects are responsible. Specifically, these authors have concluded that either electron donor or acceptor substituents on carbon in silaethylene lead to substantial Si=C bond lengthening, while substitution on silicon has little

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Table IV. π-Bond Energies for Ethylene and Its Main-Group Analogues (kcal mol^{-1})

molecule	UMP2/3-21G$^{(*)}$// UHF/3-21G$^{(*)}$	UMP2/ 6-31G*/ /UHF/ 6-31G*
From Rotational Barriers		
$H_2C{=}CH_2$	64	66
$H_2Si{=}CH_2$	35	36
$H_2Ge{=}CH_2$	31	
$H_2Sn{=}CH_2$	19	
From Disproportionation Energies		
$H_2C{=}CH_2$	67	68
$H_2Si{=}CH_2$	35	35
$H_2Ge{=}CH_2$	31	
$H_2Sn{=}CH_2$	19	

effect on double-bond length. Recent experimental data,[6] comparing bond distances in $Me_2Si{=}C(SiMe_3)[Si(Me)(t\text{-}Bu)_2]$ both free and complexed to THF, also suggest the role of solvation.

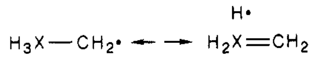
Bond lengths in the twisted biradical structures **2** are, as expected, considerably longer than in the planar (π-bonded) forms. In fact, they are close to typical single-bond lengths, e.g., experimentally 1.875 Å in $Si(Me)_4$,[4] 1.945 Å in H_3GeCH_3,[4] and 2.144 Å and $Sn(Me)_4$.[4] The calculated SiC bond length in twisted silaethylene (1.858 Å at UHF/3-21G$^{(*)}$) is close to that previously obtained by Ahlrichs and Heinzmann[8b] (1.85 Å) for the same system and also not greatly different than values reported for the corresponding triplet biradical (1.860 and 1.880 Å).[7c,23] Similarly, the calculated bond length for the singlet biradical form of germaethylene (1.956 Å) is nearly identical with that reported for the corresponding triplet state[10] (1.965 Å). Comparisons of this sort suggest that description of the singlet biradicals dealt with here as incorporating normal single linkages in which the radical sites do not significantly interact is appropriate.

The Hartree–Fock model is not expected to lead to reasonable estimates of energy differences between isomeric species with different numbers of electron pairs.[22] Indeed, at the UHF/6-31G* level the energy of the singlet biradical form of ethylene is only 40 kcal mol^{-1} above the ground-state planar species, greatly underestimating the experimental energy difference of 65 kcal mol^{-1}.[9] Similar problems occur for the remaining systems. At the UHF/3-21G$^{(*)}$ level, the singlet biradical form of stannaethylene is actually indicated to be more stable than the π-bonded structure! Note the similarity of this result to that obtained from the MNDO study on dimethylstannaethylene.[11] On the other hand, previous experience indicates that even the simplest electron correlation schemes generally provide a resonable account of the energetics of bond cleavage.[22] For example, at UMP2/6-31G*//UHF/6-31G* (Table IV), planar ethylene is shown to be 66 kcal mol^{-1} lower in energy than the corresponding twisted singlet biradical, in excellent accord with the experimental π-bond strength in this system (65 kcal mol^{-1} [9]). Lower level (UMP2/3-21G//UHF/3-21G) calculations lead to a similar result. The calculated differences in silaethylene (36 kcal mol^{-1} at UMP2/6-31G*//UH/6-31G* and 35 kcal mol^{-1} at UMP2/3-21G$^{(*)}$//UHF/3-21G$^{(*)}$) are also in apparent accord with experimental measurements for the quantity.[8d] Bond energies calculated for germaethylene and stannaethylene are somewhat smaller (31 and 19 kcal mol^{-1} at the UMP2/3-21G$^{(*)}$//UHF/3-21G$^{(*)}$ level for the two systems, respectively) and are much lower than previous experimental estimates.[8d]

Benson's method[15] for the calculation of π-bond strengths in ethylene and its main-group analogues requires evaluation of the energetics of reactions 1, involving

$$H_3X{-}CH_3 + H_2X{=}CH_2 \rightarrow H_2X^{\bullet}{-}CH_3 + H_3X{-}CH_2^{\bullet} \qquad (1)$$

consideration of the free radicals intermediate in the overall hydrogenation process, as well as the final saturated products. Structure data for these species (X = C, Si, Ge, Sn) obtained at the UHF/3-21G$^{(*)}$ level (UHF/3-21G for the ethyl free radical and ethane) are provided in Table V. The corresponding UHF/6-31G* data for the carbon and silicon systems are given in Table VI. Total energies have already presented in Table III. Note that the bond lengths connecting heavy atoms in the carbon-centered radicals $H_3X{-}CH_2^{\bullet}$ (X = Si, Ge, Sn) are significantly (0.03–0.04 Å) shorter than those in heteroatom-centered species and, in fact, are very close to those found in the corresponding twisted singlet biradicals. However, whatever extra stabilization is achieved, i.e., via participation of resonance structures of the form



$$H_3X{-}CH_2^{\bullet} \longleftrightarrow \overset{H^{\bullet}}{H_2X}{=}CH_2$$

is apparently not sufficient to offset the inherent difference in XH and CH bond dissociation energies.[24] In all three cases the heteroatom-centered radicals are more stable than the carbon-centered isomers, by 15 kcal mol^{-1} for the silicon system at UMP2/6-31G* and by 20 and 29 kcal mol^{-1} for the germanium- and tin-containing compounds at respectively[24]). Indeed, these data closely conform to experimental differences in σ-bond strengths (15, 22, and 32 kcal mol^{-1} between the CH bond energy in methane and SiH energy in silane, GeH energy in germane, and SnH energy in trimethylstannane, respectively[24]).

π-Bond strengths obtained from the Benson-type analysis (Table IV) are nearly identical with those obtained from rotational barriers. This supports the use of the procedure where barrier determinations cannot be made. Note, however, that neither of the measures of π-bond strength described here takes account of obvious differences in the underlying σ-bond energies between planar and twisted forms. That is to say, neither is able to provide a precise account of the π contribution to the total (σ + π) bond strength. Differences in σ-bond strengths (the σ bond in **1** is distorted from an optimum value, and is presumably much weaker than that in **2**), and the possibility of interaction of the two radical centers in **2** are not taken into account.

Taken as a whole, the theoretical data suggest that π-bond strengths between carbon and the elements immediately below it in the Periodic Table decrease monotonically (although not smoothly) with increasing atomic number. This observation conflicts with the experimental studies of Pietro and Hehre,[8d] at least insofar as the strengths of germanium–carbon and tin–carbon double bonds are concerned. These authors have, however, stressed that their estimates of π-bond strengths depend on a variety of experimental thermochemical data, some of it of uncertain reliability. Further work is needed to uncover the origins of the discrepancies.

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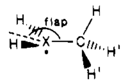
(23) Hood, D. M.; Schaefer, H. F., III *J. Chem. Phys.* **1978**, *68*, 2985.

(24) XH bond energies: CH (in CH_4) = 105 kcal mol^{-1}; SiH (in SiH_4) = 90 kcal mol^{-1} (Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246); GeH (in GeH_4) = 83 kcal mol^{-1} (Almond, M. J.; Doncaster, A. M.; Noble, P. N.; Walsh, R. *J. Am. Chem. Soc.* **1982**, *104*, 4717); SnH (in Me_3SnH) = 74 kcal mol^{-1} (Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17).

Table V. Equilibrium Geometries for Carbon- and Heteroatom-Centered Free Radicals (UHF/3-21G$^{(*)}$//UHF/3-21G$^{(*)}$)[a,b]

		X			
radical	geometrical parameter	C	Si	Ge	Sn
$H_2X^{\bullet}-CH_3$	r_{XC}	1.507	1.890	1.988	2.198
	r_{XH}	1.089	1.479	1.555	1.757
	r_{CH}	1.084	1.088	1.085	1.085
	$r_{CH'}$	1.073	1.086	1.084	1.084
	∠HCX	111.4	111.0	109.9	109.8
	∠H'CX	111.0	110.9	110.0	110.0
	flap	169.8	129.4	128.2	125.3
	∠HXH	118.1	109.2	109.1	108.0
$H_3X-CH_2^{\bullet}$	r_{XC}		1.854	1.951	2.160
	r_{XH}		1.479	1.551	1.749
	$r_{XH'}$		1.477	1.549	1.748
	r_{CH}		1.078	1.077	1.078
	∠HXC		111.6	110.9	110.6
	∠H'XC		110.1	109.8	109.6
	flap		178.4	177.9	179.5
	∠HCH		114.8	116.3	115.4
H_3X-CH_3	r_{XC}	1.542	1.884	1.979	2.187
	r_{XH}	1.084	1.478	1.551	1.750
	r_{CH}	1.084	1.087	1.084	1.084
	∠HXH	108.1	108.3	108.6	108.6
	∠HCH	108.1	107.8	108.8	108.7

[a] Bond lengths in angstroms and bond angles in degrees. [b] UHF/3-21G//UHF/3-21G for ethyl radical. [c] Geometrical parameters refer to



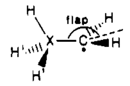


Table VI. Equilibrium Geometries for Carbon- and Silicon-Centered Free Radicals (UHF/6-31G*//UHF/6-31G*)[a]

		X	
radical	geometrical parameter	C	Si
$H_2X^{\bullet}-CH_3$	r_{XC}	1.498	1.894
	r_{XH}	1.090	1.480
	r_{CH}	1.086	1.087
	$r_{CH'}$	1.075	1.085
	∠HCX	111.9	111.0
	∠H'CX	111.2	111.0
	flap	166.6	129.4
	∠HXH	117.2	109.2
$H_3X-CH_2^{\bullet}$	r_{XC}		1.860
	r_{XH}		1.479
	$r_{XH'}$		1.477
	r_{CH}		1.078
	∠HXC		111.7
	∠H'XC		110.1
	flap		178.4
	∠HCH		114.7
H_3X-CH_3	r_{XC}	1.527	1.888
	r_{XH}	1.086	1.478
	r_{CH}	1.086	1.086
	∠HXH	107.7	107.8
	∠HCH	107.7	108.3

[a] Bond lengths in angstroms and bond angles in degrees. [b] See footnote *c* of Table V for description of geometrical parameters.

The similarity of the π-bond strengths in silaetheylene and germaethylene (in view of the much higher bond strength in ethylene and much lower strength in stannaethylene) is likely a consequence of "d-block contraction",[25] that is, the ineffective shielding provided by the 3d electrons, resulting in higher than expected effective nuclear charge for those elements immediately following the first transition series. Other properties show similar discontinuities. For example, the first ionization potentials of atomic silicon and germanium are very similar (8.15 and 7.89 eV, respectively), while that for carbon is much larger (11.26 eV) and that for tin is much smaller (7.34 eV). More relevant, the covalent radii of silicon and germanium are nearly the same (1.18 and 1.22 Å, respectively) and quite different from those of carbon (0.77 Å) and tin (1.40 Å).

Conclusion

Nonempirical molecular orbital calculations show a decreasing ordering of π-bond strengths for the series of main-group ethylene analogues $H_2X{=}CH_2$ (X = C, Si, Ge, Sn). The two measures employed (direct energy differences between planar forms and twisted singlet biradicals and energies of disproportionation of the products of hydrogen atom addition) yield nearly identical bond strengths. For ethylene and silaethylene these are in good accord with experimental determinations, while for germaethylene and stannaethylene the present theoretical values are somewhat smaller than previous experimental estimates.

Registry No. $H_2C{=}CH_2$, 74-85-1; $H_2Si{=}CH_2$, 51067-84-6; $H_2Ge{=}CH_2$, 60188-36-5; $H_2Sn{=}CH_2$, 103731-53-9.

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[25] (a) Huheey, J. E.; Huheey, C. L. *J. Chem. Educ.* **1972**, *49*, 227. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.