J. Am. Chem. Soc. 1990, 112, 2130-2137

Double Bonds and Bridged Structures in the Heavier Analogues of Ethylene

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Abstract: The singlet potential surfaces for all group 14 X_2H_4 systems are explored through ab initio SCF+CI calculations. Effective core potentials are used, which include relativistic effects for tin and lead atoms. In all cases but carbon, the bridged structures are found to be true minima with the trans isomer being favored over the cis by 2 kcal/mol. For carbon, a trans-bridged form is found to be a saddle point. The $HX_2{=}XH_2$ doubly bonded forms, planar or trans bent, are found to be true minima in all cases except for lead where it is only a saddle point. The most stable structures of Si_2H_4 and Ge_2H_4 are the trans-bent doubly bonded isomers, while the most stable structures of Sn_2H_4 and Pb_2H_4 are the trans-bridged forms. The H_3X-XH isomers lie between these two symmetrical forms and are never found to be at the absolute minimum of the surfaces. The trans-bridged structures have a rather constant binding energy with respect to 2 $XH_2(^1A_1)$ whatever the X atom (30 ± 3 kcal/mol). The stability of the bridged structures may be due to the significant ionicity of the bridges X^+-H^--X^+ in the planar four-membered rings.

The trans-bent structures of the heavier analogues of olefins disilenes, digermenes, and distannenes have now been well established both from theoretical calculations performed on the parent compounds[1-9] and from X-ray structures available for derivatives.[10-14] The case of diplumbene $H_2Pb{=}PbH_2$ has been theoretically explored at a semiempirical level only and limited to its trans-bent geometry.[15,16]

Recently a criterion has been proposed that links the existence of a trans-bent distortion at a double bond to a function of the singlet-triplet separation ΔE_{ST} of its constituent carbene parts and the double-bond energy $E_{\sigma+\pi}$.[17] According to these models the double bond in $R_2X{=}YR'_2$ should distort trans-bent when the sum of the singlet-triplet separations of the two XR_2 and YR'_2 fragments is larger than half the $\sigma+\pi$ X=Y bond energy. For a symmetrical homopolar system $R_2X{=}XR_2$ in which the two ΔE_{ST} are equal, this condition can be written

$$\Delta E_{ST} \geqslant \tfrac{1}{4}E_{\sigma+\pi} \qquad (1)$$

A second criterion, defining the existence of a direct X=Y link, be it planar or trans bent, was then proposed.[18] The double-bonded structure is only predicted to exist as long as the sum of the singlet-triplet separations is smaller than the double-bond energy. Again applied to a symmetrical homopolar system, this condition can be written

$$\Delta E_{ST} \geqslant \tfrac{1}{2}E_{\sigma+\pi} \qquad (2)$$

Table I. Singlet-Triplet Separations in XH_2 versus X=X Bond Energies[a]

	ΔE_{ST}	$^1/_4E_{\sigma+\pi}$	$^1/_2E_{\sigma+\pi}$	expected structure
$H_2C{=}CH_2$	-9	43	86	planar
$H_2Si{=}SiH_2$	18-21	18-19	35-38	trans bent (borderline)
$H_2Ge{=}GeH_2$	22	15-17	30-35	trans bent
$H_2Sn{=}SnH_2$	23	15-17	30-35	trans bent
$H_2Pb{=}PbH_2$	41	12-15	25-30	doubly bridged

[a] In kilocalories per mole. Estimates in this table are taken from the literature. For singlet-triplet splittings: CH_2, refs 22-24; SiH_2, refs 25-27; GeH_2, refs 27, 28; SnH_2, refs 27, 29, 30; PbH_2, ref 12. For $E_{\sigma+\pi}$ bond energies: C=C, ref 31; Si=Si and Ge=Ge, ref 32; Sn=Sn and Pb=Pb, estimates.

Beyond this critical value, the system is expected to lose the direct X=X link to the benefit, for instance, of a doubly bridged structure as occurs in the tetrafluoro derivatives of disilene,[19,20] digermene,[20,21] and distannene[20] (in such polar structures, electrostatics could be a further stabilizing factor). In Table I, conditions 1 and 2 are applied to the heavier analogues of ethylene $H_2X{=}XH_2$ with X = C, Si, Ge, Sn, or Pb. Examination of the results would suggest that diplumbene should not exhibit a stable Pb=Pb doubly bonded structure, a bridged geometry being more expected.

In this work we present a theoretical exploration of the X_2H_4 potential surfaces, with X varying from carbon to lead. The existence, as true minima, of trans-bent double bonds, **1**, and doubly bridged structures, **2**, and their relative energies will be the main point of concern. For the sake of completeness, the planar $H_2X{=}XH_2$ structures and the H_3X-XH carbene-like

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(1) Krogh-Jespersen, K. *J. Phys. Chem.* **1982**, *86*, 1492.

(2) Olbrich, G. *Chem. Phys. Lett.* **1986**, *130*, 115.

(3) Somasundran, K.; Amos, R. D.; Handy, N. C. *Theor. Chim. Acta* **1986**, *70*, 393.

(4) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140.

(5) Trinquier, G.; Malrieu, J. P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529.

(6) Fjeldberg, T.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1407.

(7) Nagase, S.; Kudo, T. *J. Mol. Struct. THEOCHEM* **1983**, *103*, 35.

(8) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

(9) Trinquier, G.; Malrieu, J. P. *J. Phys. Chem.*, in press.

(10) Cowley, A. H. *Polyhedron* **1984**, *3*, 389.

(11) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386.

(12) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(13) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

(14) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

(15) Gleghorn, J. T.; Hammond, N. D. A. *Chem. Phys. Lett.* **1984**, *105*, 621.

(16) Dewar, M. J. S.; Holloway, M. K.; Grady, G. L.; Stewart, J. P. *Organometallics* **1985**, *4*, 1973.

(17) Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

(18) Malrieu, J. P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916.

(19) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1986; p 249.

(20) Trinquier, G.; Barthelat, J. C., submitted for publication in *J. Am. Chem. Soc.*

(21) Huber, H.; Kündig, E. P.; Ozin, G. A.; Vandervoet, A. *Can. J. Chem.* **1974**, *52*, 95.

(22) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

(23) Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724.

(24) Schaefer, H. F., III *Science* **1986**, *231*, 1100.

(25) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348.

(26) Balasubramanian, K.; McLean, A. D. *J. Chem. Phys.* **1986**, *85*, 5117.

(27) Selmani, A.; Salahub, D. R. *J. Chem. Phys.* **1988**, *89*, 1529.

(28) Phillips, R. A.; Buenker, R. J.; Beardsworth, R.; Bunker, P. R.; Jensen, P.; Kraemer, W. P. *Chem. Phys. Lett.* **1985**, *118*, 60.

(29) Balasubramanian, K. *Chem. Phys. Lett.* **1986**, *127*, 585.

(30) Balasubramanian, K. *J. Chem. Phys.* **1988**, *89*, 5731.

(31) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 4077.

(32) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

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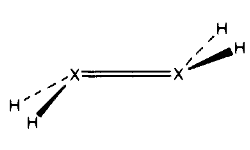

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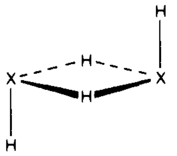

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isomers are also examined. Within a given symmetry group, the geometries are determined at an ab initio SCF-DZP level. Then a set of harmonic vibrational frequencies is calculated (at the same level of theory) in order to establish whether the structure is a true minimum, a saddle point, or neither. On these optimized geometries, relative energies are last refined through CI calculations, which introduce part of the correlation effects. Since this is—to our knowledge—the first report of ab initio calculations on the Pb_2H_4 potential surface, we wish to emphasize that the effective core potentials used in this work include, for the lead and tin atoms, part of the relativistic effects, which are so crucial for lead.[33]

After a Computational Details section, we examine the dihydrides XH_2 of the series and their singlet–triplet separations. These XH_2 species belong to the X_2H_4 potential surfaces, as dissociation products. We also examine the geometries of the monohydride diatoms XH in their $^2\Pi$ ground state and those of the tetrahydrides XH_4, in order to check the quality of our calculated geometries. Next, we discuss the X_2H_4 potential surface.

Computational Details

The SCF calculations are performed with the PSHONDOG algorithm,[34] which introduces the pseudopotentials of Durand and Barthelat[35] into the HONDO program.[36] For the tin and lead atoms, the effective core potentials take into account mean relativistic effects through mass–velocity and Darwin terms.[37] Double-ζ plus polarization (DZP) basis sets are used. The exponent for the p function on hydrogen is taken at 0.8. The exponents for the d functions are taken at 0.8 (C), 0.45 (Si), 0.25 (Ge), 0.20 (Sn), and 0.15 (Pb). The open-shell states of XH ($^2\Pi$), XH_2 ($^3B_1$), and H_3C–CH ($^3A''$) are calculated by using the UHF version of the program. The geometries are calculated with a gradient technique. Optimized geometries have energy gradient components lower than 0.0001. Harmonic vibrational frequencies are calculated through a numerical derivation of the analytical first derivatives, using a single-point differencing formula.

The configuration interaction (CI) calculations were performed with the CIPSI method.[38] This procedure combines a variational treatment of a subspace of configurations (50–80 in our examples) with a perturbational treatment of the remaining configurations generated ($\sim 10^6$). All these determinants, treated through a second-order Möller–Plesset perturbation, have a coefficient lower than 0.02 in the first-order wave function. For the triplet states of XH_2 and H_3C–CH, the starting wave functions for the CI calculations were taken from pseudo RHF SCF calculations with mean occupation numbers of the orbitals.

Note that the spin–orbit coupling is not introduced in the present calculations. Its effects may deepen shallow minima on surfaces involving heavy atoms. For PbH_2, it was found to change appreciably the geometry of the $^3B_1$ triplet state. We expect that spin–orbit coupling should not significantly alter our *singlet* Pb_2H_4 surface, although it might induce inflections in those parts where the surface is flat, such as near the trans-bent region.

Table II. Results for Group 14 Dihydrides[a]

	$^1A_1$		$^3B_1$			
	X-H	HXH	X-H	HXH	ΔE_{ST}(SCF)	ΔE_{ST}(CI)
CH_2	1.106	102.5	1.082	130.7	−29.5	−14.0–12.7[b]
SiH_2	1.508	93.7	1.469	118.4	3.9	16.7
GeH_2	1.597	93.0	1.544	118.7	9.6	21.8
SnH_2	1.768	92.5	1.711	117.3	14.5	24.8
PbH_2	1.832	92.0	1.763	119.2	26.3	34.8

[a] Bond lengths in angstroms, bond angles in degrees, and relative energies in kilocalories per mole. [b] Refined treatment of the CI through an extrapolation technique.

Table III. Calculated Bond Length (in Å) in Group 14 Hydrides

		SCF(DZP)	exptl[a]
C-H	CH_4	1.09	1.09
	CH	1.12	1.12
	CH_2	1.11	1.11
	CH_2 ($^3B_1$)	1.08	1.07
Si-H	SiH_4	1.47	1.48
	SiH	1.51	1.52
	SiH_2	1.51	1.52
Ge-H	GeH_4	1.55	1.53
	GeH	1.60	1.59
	GeH_2	1.60	
Sn-H	SnH_4	1.71	1.71
	SnH	1.77	1.78
	SnH_2	1.77	
Pb-H	PbH_4	1.74	1.75
	PbH	1.84	1.84
	PbH_2	1.83	

[a] The experimental bond lengths are taken from ref 42 for the diatoms and from ref 43, except for CH_2 (ref 44), GeH_4 (ref 45), and PbH_4 (value deduced from the experimental bond lengths in PbH, SnH, and SnH_4, ref 46).

Group 14 Hydrides

The optimized geometries for the group 14 dihydrides XH_2 in their $^1A_1$ and $^3B_1$ states are reported in Table II, together with their singlet–triplet separations. The geometries are in agreement with other SCF-calculated ones for CH_2, SiH_2, GeH_2, and SnH_2. For PbH_2, our calculated bond lengths are shorter by 0.06 Å than those calculated in ref 30 but are comparable to those in ref 39 (see also, ref 33c). At our level of description, the energy of the $^1A_1$ singlet states is underestimated with respect to the $^3B_1$ triplet states for CH_2 and SiH_2 for which accurate calculations are available. For CH_2, $\Delta E_{ST} = -9$ kcal/mol.[22-24] For SiH_2, ΔE_{ST} has been calculated at 18–21 kcal/mol.[25-27] In order to trace the singlet energy underestimation, we performed a refined CI treatment for CH_2, using a technique of extrapolation that evaluates a variational energy for the full configurational space.[40] With this procedure, ΔE_{ST} is reduced to −12.7 kcal/mol, which is quite acceptable in regard to other treatments within the kind of basis set we use.[41]

The ΔE_{ST} values are in better agreement with those previously published for GeH_2 (22 kcal/mol)[27,28] and SnH_2 (23–24 kcal/mol).[27,30] For PbH_2, if we compare with the value calculated *without* spin–orbit coupling in ref 30, ΔE_{ST} = 33.2 kcal/mol, the agreement is good. In summary, we can say that our procedure provides a reliable description of the potential surfaces, especially

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(33) (a) Balasubramanian, K.; Pitzer, K. S. In *Ab initio Methods in Quantum Chemistry I*; Lawley, K. P., Ed. *Adv. Chem. Phys.* **1989**, *67*, 287. (b) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (c) Almlof, J.; Faegri, K., Jr. *Theor. Chim. Acta* **1986**, *69*, 437. (d) Pélissier, M. Thesis. Université Paul-Sabatier, Toulouse, 1980. (e) Balasubramanian, K. *J. Phys. Chem.* **1989**, *93*, 6585.

(34) Pélissier, M.; Komiha, N.; Daudey, J. P. *J. Comput. Chem.* **1988**, *9*, 298.

(35) Durand, Ph.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283.

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

(37) Barthelat, J. C.; Pélissier, M.; Durand, Ph. *Phys. Rev. A* **1981**, *21*, 1773.

(38) Daudey, J. P.; Malrieu, J. P. In *Current Aspects of Quantum Chemistry*; Carbo, T., Ed.; Elsevier: Amsterdam, 1982; p 35.

(39) Schwerdtfeger, P.; Silberbach, H.; Miehlich, B. *J. Chem. Phys.* **1989**, *90*, 762.

(40) Evanglisti, S.; Daudey, J. P.; Malrieu, J. P. *Chem. Phys.* **1983**, *75*, 91.

(41) Bauschlicher, C. W.; Taylor, P. R. *J. Chem. Phys.* **1986**, *85*, 6510.

(42) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.

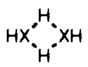
(43) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(44) Herzberg, G.; Johns, J. W. C. *J. Chem. Phys.* **1971**, *54*, 2276.

(45) *Tables of Interatomic Distances*; Special Publication 18; The Chemical Society: London, 1965.

(46) Desclaux, J. P.; Pyykkö, P. *Chem. Phys. Lett.* **1974**, *29*, 534.

Table IV. SCF-Calculated Geometries for the Stationary Points of the X_2H_4 Potential Energy Surfaces[a]

isomers		parameters	C		Si		Ge		Sn		Pb	
$H_2X{=}XH_2$	planar	X=X	1.322		2.117		2.245		2.537		2.572	
		X—H	1.085		1.465		1.534		1.696		1.722	
		HXH	116.6		115.7		115.4		114.7		116.0	
$H_2X{=}XH_2$	trans bent	X=X					2.315		2.712		2.999	
		X—H					1.547		1.728		1.800	
		HXH					109.5		103.2		97.1	
		θ					36.5		48.9		56.3	
	(trans and cis)[b]	$X—H_1$	1.243	1.282	1.654	1.659	1.775	1.781	1.933	1.940	2.038	2.045
		X···X	1.655	1.430	2.585	2.603	2.798	2.818	3.090	3.114	3.253	3.278
		H_1XH_1	96.5	83.0	77.2	76.7	75.9	75.4	73.9	73.2	74.1	73.5
		XH_1X	83.5	67.8	102.8	103.3	104.1	104.6	106.1	106.8	105.9	106.5
		puckering[c]		83.6		1.4		0.8		1.1		2.2
		$X—H_2$	1.095	1.099	1.502	1.499	1.593	1.587	1.766	1.758	1.834	1.821
		H_1XH_2	97.8	134.9	89.3	93.3	88.7	92.1	87.6	91.2	87.8	91.0
		φ	101.7	160.5	89.1	94.2	88.4	92.7	87.0	91.6	87.2	91.2
H_3X-XH ($^1A'$)		X—X	1.487	1.487[d]	2.399		2.574		2.886		2.959	
		$X—H_1$	1.105	1.082	1.508		1.596		1.767		1.829	
		$X—H_2$	1.091	1.093	1.477		1.553		1.721		1.763	
		$X—H_3$	1.101	1.096	1.481		1.555		1.721		1.760	
		XXH_1	105.3	130.7	92.2		91.2		89.9		88.5	
		XXH_2	114.2	110.4	112.0		112.4		112.8		114.9	
		XXH_3	109.2	111.7	109.9		110.5		111.5		112.1	
		H_3XH_3	105.2	107.7	108.6		108.0		107.3		106.0	

[a] In angstroms and degrees. See Figure 1 for the labeling. [b] The two columns refer to the trans and cis isomers, respectively. [c] For the cis isomers only. Supplement of the dihedral angle between the two H_1XH_1 planes of the ring. [d] This column refers to the $^3A''$ state of H_3 C–CH.

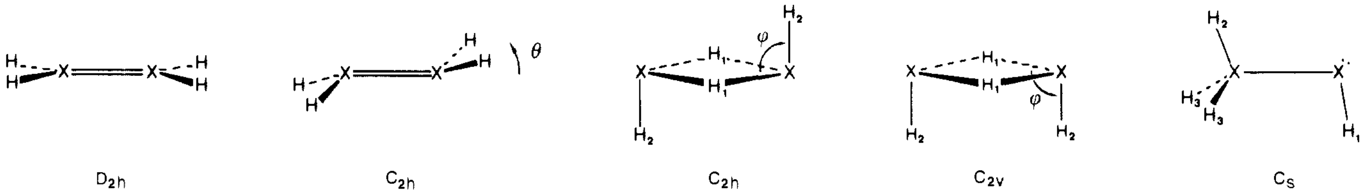


Figure 1. Definition of the geometrical parameters.

those including the heavy atoms, which is the main object of this work.

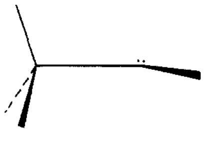
To complete the geometry tests, we determined, still at the SCF level, the X–H bond lengths in XH_4 (T_d) and in the $^2\Pi$ ground state of the diatoms XH. For most of these bond lengths, experimental values are available. We gathered the bond lengths for group 14 mono-, di-, and tetrahydrides in Table III. To an accuracy of a hundredth of an angstrom, the SCF-DZP calculations have a remarkable ability to reproduce these bond lengths. Of course we know that this is due to a balance of errors between the lack of base completeness at the Hartree–Fock level and the lack of accounting for all correlation effects. Note in particular that since the bond lengths in singlet XH_2 happen to be close to those in XH, our calculated Pb–H bond length in singlet PbH_2 (1.83 Å) is quite reasonable.

X_2H_4 Potential Energy Surfaces

Except for H_3C–CH, which is triplet in its ground state, the H_3X–XH isomers have singlet ground states. This is why we have considered only $^1A'$ singlet species for H_3Si–SiH, H_3Ge–GeH, H_3Sn–SnH, and H_3Pb–PbH. For methylmethylene, both states $^1A'$ and $^3A''$ have been calculated, but the discussion about the whole potential surface will only concern the $^1A'$ singlet state.

Since the geometries are determined at the Hartree–Fock level, it is important to evaluate whether inclusion of correlation effects could change the nature of our SCF stationary points. The very flat surface relative to trans bending in disilene is a case where inclusion of correlation effects may change a minimum (the D_{2h} planar form) into a saddle point and create a minimum (the C_{2h} trans-bent form) from a nonstationary point. At our SCF-DZP level of description, we get a planar disilene in agreement with other results from the literature.[3] However, it is well-known that the inclusion of some correlation effects gives a trans-bent disilene, with the planar structure being the transition state between the two trans-bent forms. This case may be considered as a special case, due to the very flat surface corresponding to this trans-wagging coordinate. In digermene and distannene, correlation effects no longer change the shape of the bending curves since they are less flat,[5-9]

A less trivial case is that of singlet methylmethylene (or ethylidene) H_3C–CH. This structure, in its preferred C_1 geometry, **3**, is a true minimum at the SCF level.[47] The barrier for the



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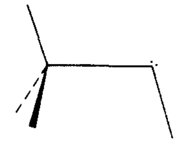

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methylmethylene → ethylene rearrangement, calculated at 12 kcal/mol at the SCF level, disappears when both correlation is included at the highest level and zero-point energy corrections are taken into account.[48] Therefore, it is likely that the singlet methylmethylene, in its C_s structure, **4**, is only the transition state for degenerate 1,2 hydrogen rearrangement in ethylene.[47-49] This case can also be considered as a special case since the reaction $H_3C{-}CH \rightarrow H_2C{=}CH_2$ is very exothermic (ΔE = 79 kcal/mol). With silicon, the analogous isomerization results in an energy benefit of only 5–8 kcal/mol.[1,2,50,51] The corresponding barrier has been calculated to lie at 21 kcal/mol above silylsilylene at the SCF level and still at 12 kcal/mol at the best level of correlation description.[50] Therefore, there is no doubt that singlet silylsilylene is a true minimum on the potential energy surface,

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(47) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 145.

(48) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

(49) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986; p 426.

(50) Krogh-Jespersen, K. *Chem. Phys. Lett.* **1982**, *93*, 327.

(51) Kohler, H. J.; Lischka, H. *Chem. Phys. Lett.* **1984**, *112*, 33.

Table V. Harmonic Vibrational Frequencies (cm^{-1}) for the Planar Forms

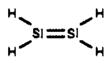
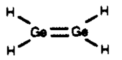
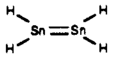
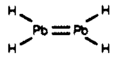
							
b_{2g}	105	b_{2g}	286 i	b_{2g}	417 i	b_{2g}	666 i
b_{2u}	417	a_g	377	a_g	262	a_g	189
a_u	586	b_{2u}	381	b_{2u}	322	b_{2u}	305
b_{1u}	638	a_u	561	a_u	470	b_{1g}	451
a_g	639	b_{1g}	577	b_{1g}	473	a_u	467
b_{1g}	658	b_{1u}	590	b_{1u}	506	b_{1u}	494
b_{3u}	962	b_{3u}	867	b_{3u}	725	b_{3u}	646
a_g	1043	a_g	953	a_g	816	a_g	782
b_{3u}	2382	b_{3u}	2238	b_{3u}	2097	b_{3u}	1968
a_g	2394	b_{1g}	2241	b_{1g}	2101	b_{1g}	1987
b_{1g}	2404	b_{2u}	2247	b_{2u}	2105	a_g	1992
b_{2u}	2412	a_g	2252	a_g	2112	b_{2u}	1992

Table VI. Harmonic Vibrational Frequencies (cm^{-1}) for the Trans-Bent Forms

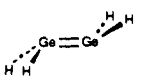
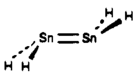
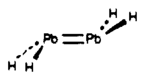
					
a_g	257	a_g	162	b_u	112 i
a_u	347	a_u	259	a_g	72
b_u	446	b_u	259	a_u	173
a_g	492	a_u	386	a_u	273
a_u	520	b_g	452	b_g	321
b_g	579	a_g	527	a_g	501
b_u	936	a_g	833	a_g	807
a_g	959	b_u	841	b_u	821
b_g	2179	b_g	1987	b_g	1742
b_u	2183	b_u	1997	a_g	1744
a_g	2190	a_g	1998	b_u	1748
a_u	2191	a_u	2002	a_u	1766

Table VII. Harmonic Vibrational Frequencies (cm^{-1}) for the Trans-Bridged Forms

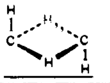
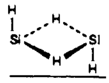
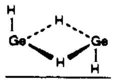
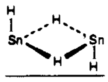
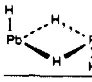
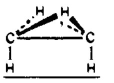
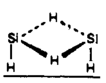
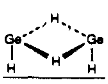
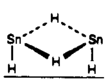
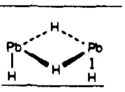
									
b_u	945 i	b_u	371	a_g	236	a_g	178	a_g	121
a_g	699	a_g	408	b_u	310	b_u	264	b_u	210
b_g	873	a_u	765	a_u	673	a_u	567	a_u	517
b_u	1046	a_g	921	a_g	804	a_g	674	a_g	604
a_u	1354	b_g	987	b_g	866	b_g	820	b_g	745
a_g	1434	b_u	1000	b_u	911	b_u	863	b_u	797
b_u	1565	a_u	1371	b_g	1178	a_u	1137	b_g	982
b_g	2057	b_g	1438	a_u	1200	b_g	1234	a_u	1007
a_u	2342	b_u	1590	b_u	1379	b_u	1413	b_u	1217
a_g	2521	a_g	1769	a_g	1576	a_g	1478	a_g	1291
a_g	3183	a_g	2187	a_g	1990	a_g	1867	a_g	1654
b_u	3200	b_u	2200	b_u	2005	b_u	1882	b_u	1674

Table VIII. Harmonic Vibrational Frequencies (cm^{-1}) for the Cis-Bridged Forms

									
b_1	1826 i	a_1	406	a_1	235	a_1	177	a_1	121
a_2	1109 i	a_1	445	a_1	380	a_1	339	a_1	294
b_2	791	a_2	694	a_2	614	a_2	510	a_2	473
a_1	913	b_1	849	b_1	741	b_1	616	b_1	552
a_1	1186	b_2	999	b_2	901	b_2	813	b_2	748
a_2	1302	a_1	1040	a_1	941	a_1	867	a_1	799
b_1	1327	a_2	1349	a_2	1080	b_2	1119	a_2	921
a_1	1559	b_2	1358	b_2	1184	a_2	1175	b_2	990
b_2	2447	b_1	1526	b_1	1324	b_1	1378	b_1	1189
a_1	2461	a_1	1762	a_1	1570	a_1	1471	a_1	1285
b_1	3154	b_1	2223	b_1	2028	b_1	1909	b_1	1704
a_1	3190	a_1	2247	a_1	2052	a_1	1930	a_1	1729

as obtained at the SCF level. Consequently, except for singlet methylmethylene and disilene, we shall trust the nature of our stationary points as obtained at the SCF level. Let us point out, lastly, that the geometries for all singlet H_3X–XH will be considered in the staggered conformation **4** since this is the preferred geometry for silylsilylene[50] and most probably for its heavier analogues (**3** and **4** are, in any case, nearly degenerate in energy for singlet methylmethylene).[47]

The SCF optimized geometries are given in Table IV and Figure 1. For the most interesting points, the calculated sets of vibrational frequencies are given in Tables V–VIII. The relative energies for the X_2H_4 isomers, including the dissociation product $2XH_2$ ($^1A_1$), are listed in Table IX, at both SCF and CI levels. The zero-point energies, which are very close for all the isomers of a given family, are not taken into account. The SCF/CI comparison is interesting only from a technical point of view. For the physical discussion, we shall only consider the CI-calculated relative energies.

1. Stationary Points. **C_2H_4.** At the SCF level, only two true minima are found: the ethylene structure, which is by far the absolute minimum, and the methylmethylene structure (both singlet and triplet). The C_{2h} trans-bridged structure is a saddle point with one negative eigenvalue in the second-derivative matrix. The C_{2v} cis-bridged structure is a critical point with two negative eigenvalues. We must note that these bridged structures have a special status compared to the bridged structures of the heavier analogues. These are not true minima on the C_2H_4 potential surface and their geometries are different in nature from their heavier analogues, as can be seen in Table IV. In particular the cis-bridged form of C_2H_4 has a normal C–C bond and a large puckering of the cycle, **5**, unlike the nearly planar rings of the stable heavier analogues, **6**. We shall discuss these points in more detail later. Also note that these stationary points are very high in energy on the C_2H_4 surface. Considering that more refined treatments would suppress singlet methylmethylene as a true minimum (see above), one can conclude that the real physical C_2H_4 potential energy surface exhibits a single true minimum that corresponds to the stable structure of ethylene.

5

6

Si_2H_4. This potential surface has previously been determined by Kohler and Lischka at the same level of description.[51] Our results are in agreement with theirs. At the SCF-DZP level, disilene is found to be planar, i.e., there is no stationary point corresponding to a trans-bent geometry. The two bridged structures, cis and trans, and silylsilylene are found to be true minima. Since, at a higher level of description, disilene is found to be trans bent, we conclude that the real physical Si_2H_4 potential energy surface exhibits four kinds of true minima and a saddle point corresponding to the low barrier to planarity of trans-bent disilene.

Ge_2H_4. The trans-bent structure, the two bridged structures, and the germylgermylene structure are found to be real minima. The planar digermene form is the transition state for interconverting the two trans-bent forms.

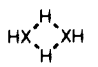
Sn_2H_4. As in the case of Ge_2H_4, the four main structures are found to be true minima while planar distannene is a saddle point.

Pb_2H_4. The two bridged forms and the plumbylplumbylene form are found to be true minima. Planar diplumbene is a saddle point with a single imaginary frequency corresponding to trans bending, **7**, as for the Ge and Sn surface. Quite remarkably, the trans-bent form is no longer a local minimum, but a saddle point with a single imaginary frequency corresponding to deformation

7

8

Table IX. Calculated Relative Energies (in kcal/mol)

		C_2H_4		Si_2H_4		Ge_2H_4		Sn_2H_4		Pb_2H_4	
		SCF	CI	SCF	CI	SCF	CI	SCF	CI	SCF	CI
$2\ XH_2\ (^1A_1)$		173.8	192.0	48.5	53.7	38.9	35.9	33.3	33.2	30.6	28.7
$H_3\ X{-}XH\ (^1A')$	C_s	73.4	79.1 65.3^a	0.1	9.8	0	2.4	1.3	7.0	14.8	17.5
	C_{2v} cis	145.3^c	140.3	24.8	25.2	16.6	11.6	2.1	2.3	2.1	2.0
	C_{2h} trans	166.9^b	164.7	22.6	22.5	14.8	9.0	0	0	0	0
$H_2\ X{=}XH_2$	C_{2h} trans bent					8.7	0	14.1	9.1	24.0^b	23.9
$H_2\ X{=}XH_2$	D_{2h} planar	0	0	0	0	10.6^b	3.2	23.2^b	18.5	53.6^b	43.7

^{a} $^3A'$ triplet state. ^{b}Saddle points. ^{c}Critical point of index 2.

Table X. Nature of the X_2H_4 Stationary Points with the Group 14 Elements^a

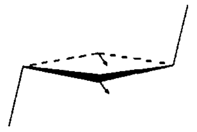
					
C	ATM		SP	CP2	SP
Si	SP	ATM	TM	TM	TM
Ge	SP	ATM	TM	TM	TM
Sn	SP	TM	ATM	TM	TM
Pb	SP	SP	ATM	TM	TM

^{a}Abbreviations: ATM, absolute true minimum; TM, true minimum; SP, saddle point (=transition state); CP2, critical point of index 2.

8.[52] So, the prediction that a doubly bonded structure should no longer exist for diplumbene seems to be satisfied. Note however that relations 1 and 2 do not account for the existence of bridged forms for Si_2H_4, Ge_2H_4, and Sn_2H_4.

Finally, we have summarized in Table X the nature of all the bound structures on the X_2H_4 potential surfaces. The geometries of the bridged structures will be commented on later. Let us point out here some geometrical trends for the other isomers along the group 14 series. The planar structures have rather constant HXH angles (115–117°) and have X=X distances 11–13% shorter than the X–X distances in $H_3X{-}XH$. The wagging angles in the trans-bent doubly bonded structures increase steadily from germanium to lead. Correlation effects are known to increase these angles and the likely values of θ are 36° for Si, 40–42° for Ge and 50° for Sn.[9] With respect to planar $H_2X{=}XH_2$, the X=X distance in the trans-bent form is lenghened by 3%, 6%, and 24% in digermene, distannene, and diplumbene, respectively. In $H_3X{-}XH$, the X–X distances are longer than these in $H_3X{-}XH_3$, except for carbon where the CC distance in ethane is longer than that in $H_3C{-}CH$. Note that the XXH_1 angles in singlet $H_3X{-}XH$ are close to the HXH angles in singlet XH_2 but they are below 90° in H_3SnSnH and H_3PbPbH.

2. Relative Energies and Shapes of the Surfaces. The C_2H_4 singlet potential energy surface is well-known.[47-49] There is a deep single true minimum for ethylene, a structure stabilized by the very strong $2p_z$–$2p_z$ electronic delocalization. Singlet methylmethylene is the transition state for hydrogen scrambling in ethylene and lies high in energy at 70–80 kcal/mol above ethylene. The trans-bridged structure, which is also a saddle point, lies even higher in energy, at 165 kcal/mol above ethylene. The cis-bridged structure, which is a critical point of index 2, lies below the trans-bridged structure, but still high in energy at 140 kcal/mol above ethylene. These stationary points have little interest for ethylene since they are very high in energy, but with heavier elements they are true or absolute minima. A look at the imaginary frequencies for the bridged C_2H_4 isomers may help to figure out connections between all the stationary points. The imaginary frequency for trans-bridged C_2H_4 corresponds to the b_{2u} movement **9**. This suggests that the trans-bridged arrangement can be regarded as the midpoint (here a transition state) on the least-motion C_s isomerization of degenerate staggered singlet methylmethylenes, **10**. For heavier analogues this intermediate is a true minimum or even the absolute minimum. The second imaginary frequency for cis-bridged C_2H_4 corresponds to the a_2 vibration **11**. This is a direct relaxation toward trans-bent and planar ethylene. The first imaginary frequency for cis-bridged C_2H_4 corresponds to the b_1 deformation **12**, which can be seen as the midpoint along the least-motion C_s isomerization of the two degenerate eclipsed singlet methylmethylenes, **13**. Again, this is of little interest in itself for the C_2H_4 surface since none of these forms is a true minimum and they are all very high in energy. However, as the present results show, all these forms happen to be true minima for the heavier analogues, with the trans-bridged form being even the absolute minima for the Sn_2H_4 and Pb_2H_4 potential surfaces. This is why we think that these pathways across the potential surfaces will help us to connect the stationary points and to understand the whole surfaces. Let us now comment on the relative energies for the heavier X_2H_4 isomers.



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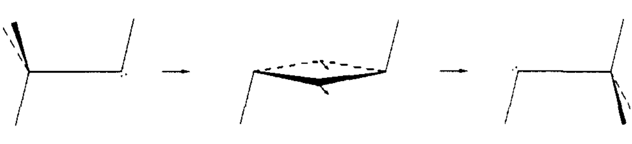

10

11

12

13

First, we can settle, once and for all, the question of the energy differences between the cis and trans forms of the bridged isomers. The trans-bridged form is always found to be more stable than the cis-bridged form by ~2 kcal/mol. This quantity is remarkably constant whatever the atom (except for carbon, which is a quite different case) and whatever the level of description. It also holds for Ge_2F_4[20] (see also refs 19 and 51). Such a weak energy difference is not easy to explain, but we will point out that for these

---

[52] (52) Letting the optimization go according to this mode leads to another saddle point, of C_s symmetry, in which the Pb–PbH$_2$ part is nearly planar and the left-hand-side H_2Pb is tilted below the PbPb bond. Distorting in turn this saddle point leads to a completely unsymmetrical C_1 stationary point with a single hydrogen bridge and a rather short Pb–Pb distance (2.94 Å). According to the force field calculated at the closed-shell RHF level, this form would be a real minimum. This deserves to be explored at a most refined level and we will not, in this work, pay attention to this puzzling secondary minimum.

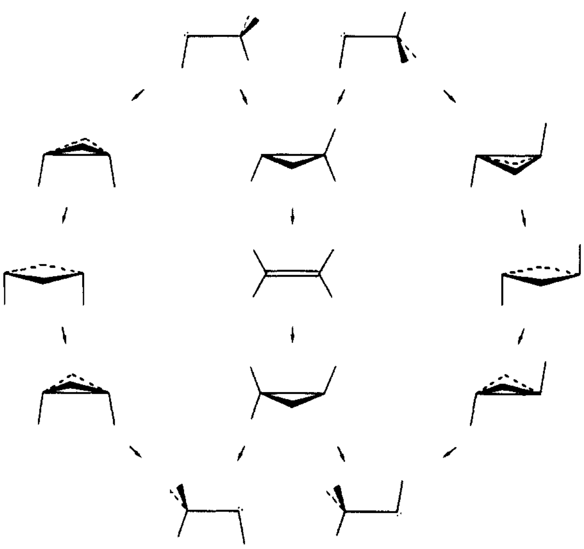

Figure 2. A possible connection of the various stationary points.

significantly polar systems the trans arrangement of the extracyclic X–H bonds is expected to be preferred over the cis arrangement.

On the Si_2H_4 surface, the trans-bent disilene form is the absolute minimum. The silylsilylene form lies ~9 kcal/mol higher in energy (the most refined calculations give 5–6 kcal/mol for this energy difference).[3] Lastly, the trans doubly bridged structure lies 22 kcal/mol above disilene. Our results are in good agreement with those of Kohler and Lischka at the SCF level.[51] However, we find that the CI does not stabilize the bridged form with respect to the disilene form whereas they found a 5 kcal/mol relative stabilization. For the Ge_2H_4 potential surface, a similar stability ordering is obtained, with relative energies 0, 2, and 9 kcal/mol. For the Sn_2H_4 potential surface, we have a reverse ordering, with the bridged structure being the absolute minimum and the trans-bent form being the least stable isomer. Relative energies are calculated at 0, 7, and 9 kcal/mol. For the Pb_2H_4 potential surface, there are only two true minima. The bridged form is preferred over the plumbylplumbylene form by 17 kcal/mol. The trans-bent form is a saddle point lying 24 kcal/mol above the bridged form.

Let us try to picture these singlet potential surfaces using the above-mentioned topological links between stationary points. In Figure 2 we propose one possible topological scheme of the part of the X_2H_4 potential surface we are interested in. Starting from a staggered C_s form of H_3X–XH (top right), its degenerate isomer (bottom right) can be reached either through (i) a nonsymmetrical C_s pathway with the $H_2X{=}XH_2$ planar or trans-bent form as intermediate (middle) or through (ii) a more concerted C_1 pathway with the trans-bridged form as intermediate (right). A similar double route can be schematized for the isomerization of the eclipsed C_s form of H_3X–XH (top left). In this case, the pathway through the $H_2X{=}XH_2$ intermediate is common (middle) while the pathway through a bridged intermediate involves the cis-bridged form (left). When X is not carbon, the eclipsed form is slightly higher in energy than the staggered form and the cis-bridged form is slightly higher in energy than the trans-bridged form (expectedly by comparable energy differences). So the two pathways, through the trans-bridged (right) or cis-bridged (left) intermediates, should be associated with similar energy profiles. We have plotted in Figure 3 the energy shapes along the two pathways (middle and right parts) of Figure 2, which illustrate and clarify the differences across the group 14 column. It should not be forgotten that this is a scheme devoted to illustrating these differences; the real surface is more complicated and there are other ways of connecting the stationary points. In Figure 3 we use the CI-calculated energy differences of Table X, together with arbitrary barriers around true minima. We have included the C_2H_4 surface for comparison, although in this case the cis-bridged critical point is ~24 kcal/mol below the trans-bridged one, but still high in energy.

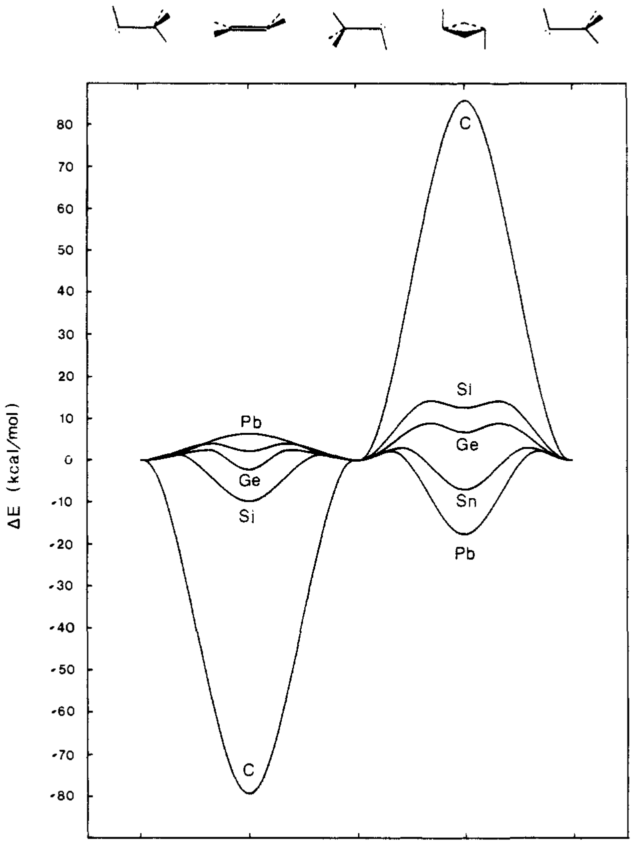

Figure 3. Schematic view of the potential surfaces. The horizontal axis is an arbitrary coordinate related to the pathways of Figure 2. Zero energy corresponds to the H_3X–XH forms and is common to all surfaces.

Figure 3 makes it clear that on going down the group 14 column from carbon to lead, the bridged structures are favored while the double bonds are disfavored. The germanium/tin gap is singular insofar as before it the double bonds are the absolute minima on the surfaces and beyond it the trans-bridged forms are the absolute minima. The H_3X–XH structure is never found to be the absolute minimum at the CI level. Figure 3 also pictures the remarkable difference between carbon and its heavier group 14 analogues, with the priviledged status of $2p_z$–$2p_z$ π bonding.

3. Dissociation into Two XH_2. The natural dissociation product of the planar double bond $H_2X{=}XH_2$ is a pair of $^3B_1$ triplet XH_2 species. The natural dissociation product of a trans-bent double bond is a pair of $^1A_1$ singlet XH_2 species. Since these are the ground states for all XH_2 (except for methylene), let us look at their relative positions on the X_2H_4 potential surfaces. The corresponding energies are given in Table IX. The results are made easier to analyze and to interpret if the zero energy is chosen as that of the two separated XH_2 singlet fragments. This is done in Figure 4, which reads as follows: At the right-hand side lies the common zero origin corresponding to $2XH_2$ ($^1A_1$). Moving to the left, these fragments are brought together to form the trans-bridged structures; then, following an arbitrary coordinate, the trans-bent forms are reached; after, still moving to the left, the trans-bent forms are brought to planarity; lastly, on the left asymptotes, the planar forms are dissociated into their "natural" dissociation products $2XH_2$ ($^3B_1$). Here also the barriers separating the trans-bent forms and the bridged froms are chosen arbitrarily. Note that over the whole arbitrary coordinate, the saddle points are now plateau points (do not pay too much attention to that part of the Pb curve running between the trans-bent form and the bridged form; a monotonic curve has been plotted but there might be a local minimum somewhere in that region). In this scheme we consider disilene as trans bent, with a weak barrier to planarity. Figure 4 shows that with respect to two singlet XH_2 fragments, the doubly bonded structures are more or less stable depending on the X atom (with a remarkable stability for carbon). In contrast to this, the bridged structures happen to have

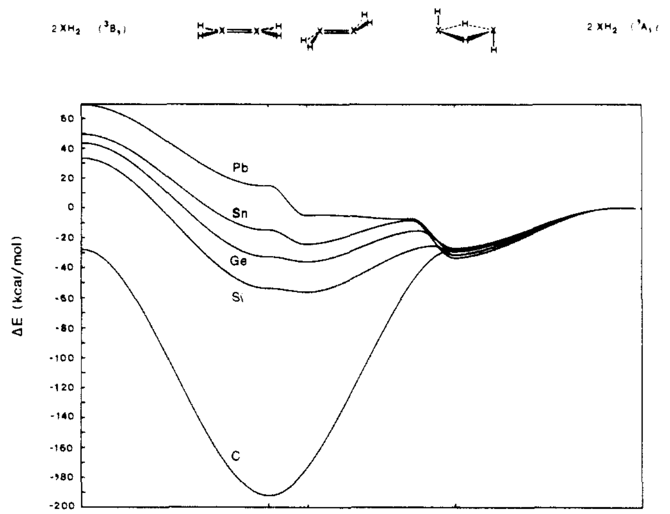

Figure 4. Another view of the potential surfaces, connecting the doubly bonded and doubly bridged structures to the dissociation products $2XH_2$. The horizontal axis is an arbitrary coordinate. Zero energy is common to all surfaces and corresponds to $2XH_2$ ($^1A_1$) (far right).

a fairly constant binding energy relative to $2XH_2$ ($^1A_1$) whatever the X atom ($\Delta E = 30 \pm 3$ kcal/mol). Quite interestingly, this is also satisfied for carbon, the trans-bridged structure of which is only a saddle point. This singular property of the trans-bridged structures suggests a special kind of bonding in these species, for instance one in which electrostatic contributions could be predominant. This point will be addressed in the next section. Note in Figure 4 that, for lead, the bridged structure is the only minimum among the symmetrical structures. It can also be noticed that as X becomes heavier, the ΔE_{ST} in XH_2 becomes larger (left part) with, here also, the unique triplet ground state for CH_2. The energy benefit due to the coupling of two triplet XH_2 fragments into a planar olefin structure $H_2X{=}XH_2$ is a possible measure of intrinsic $\sigma{+}\pi$ X=X bond energy. According to this technique, the following values are obtained for $E_{\sigma+\pi}$:

bond	$E_{\sigma+\pi}$, kcal/mol
C=C	164
Si=Si	87
Ge=Ge	76
Sn=Sn	64
Pb=Pb	55

These binding energies decrease regularly from silicon to lead, while that of carbon is much larger.

4. Structures of the Bridged Forms. Except for cis-bridged C_2H_4, which exhibits a short C–C bond, all bridged structures have X···X bonds longer than normal X–X single bonds including those in $R_3X{-}XR_3$ and in metals (except for metallic lead, which has a Pb–Pb interatomic distance of 3.5 Å).[53] The calculated overlap populations between the X atoms are found to be negative in all the bridged compounds (this index spans from −0.03 in Pb_2H_4 to −0.09 in Si_2H_4). Despite the arbitrariness of Mulliken population analyses and because of the rather long X···X distances, we are tempted to conclude there is *no direct* XX bonding in such rings (this is why no XX bond is drawn in any bridged structure).[54]

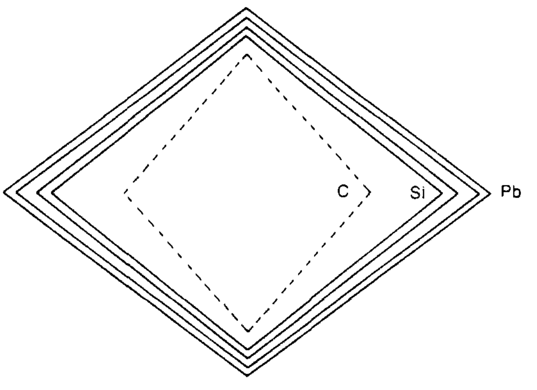

Figure 5. Geometries of the planar rings in the trans-bridged structures. From inside to outside: C_2H_4, Si_2H_4, Ge_2H_4, Sn_2H_4, and Pb_2H_4.

Concerning the structure of the ring itself, we must first recall that the planarity of the X_2H_2 ring is imposed by the C_{2h} symmetry in the trans-bridged structures while this is no longer true for the cis-bridged isomers. Actually, they are slightly puckered, always on the side of the extracyclic XH bonds. This can be accounted for by the repulsion between the two lone pairs which, for the cis isomers, are both located on the same side of the ring plane, opposite to the extracyclic X–H bonds. The lone pair–lone pair repulsion therefore seems to prevail over HH repulsion.

The shapes of these planar cycles exhibit remarkable similarities, except for carbon. The quadrilaterals are rhombuses with the acute angles on the X centers, except for carbon (see Figure 5). Simple electrostatic arguments can account for these shapes. In all cases but carbon the hydrogens of the ring bear significant negative charges (−0.2e to −0.3e) whose intensities remain about half those of the positive charges at the X centers (+0.3e to +0.5e). From this naive scheme, the XX repulsion should prevail over the HH one and impose the XX axis as the long diagonal. Such a scheme of alternating charges on a planar four-membered ring was also encountered on cyclodiphosphazene $(H_2PN)_2$ where the larger charges are located on the nitrogen atoms, inducing the acute angle on them.[58] As can be seen in Figure 5, the case of trans-bridged C_2H_4 does not follow this explanation. Although the charges on the hydrogens are still about half those on the carbons, they are smaller in intensity and are of reversed signs (C^-H^+). Presumably, the singular structure of trans-bridged C_2H_4 is rather due to its saddle-point character. Note that the cis-bridged structure of C_2H_4, **5**, which is a stationary point of index 2, has a clear C–C bond and has nothing to do with these planar bridged forms.

The intracyclic X–H distances in the bridged structures correspond to a lengthening of 9–12% with respect to the bond lengths in singlet XH_2. The extracyclic X–H distances keep their values of singlet XH_2. In the trans isomers, the H_1XH_2 angles are 5° smaller than these in singlet XH_2, and they are about equal to the angles between the ring plane and the extracyclic XH bonds. They lie in the range 87–89°. Note that this is smaller than 90° and makes these structures more compact. In the cis isomers, these angles lie in the range 91–94°. The cis repulsion between the extracyclic XH bonds is presumably responsible for the larger values of H_1XH_2 and φ.

The bonding in the bridged structures is governed by a three-center two-electron scheme, quite analogous to that which holds in diborane and its heavier analogues.[59] The unsaturated X_2H_4 systems, **14**, are isoelectronic with the saturated electron-deficient hydrides of group 13 Y_2H_6, **15**. In all cases, there is an excess of electrons on the bridge hydrogens.[55] As with halogen bridges, highly ionic $X^+{-}H^-{-}X^+$ or $Y^+{-}H^-{-}Y^+$ bonds are found from SCF molecular orbital calculations. The stabilization of the planar ring by charge alternation is illustrated by the increase in the X–H bond polarity when going from isolated XH_2 to the

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(53) (a) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, U.K., 1975; p 728, 1022. (b) In some anionic clusters, one can find rather long distances (up to 3.2 Å) for Sn–Sn and Pb–Pb: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; p 457.

(54) On the difficulty of settling the question of direct MM bonding interactions in M–X–M doubly bridged compounds with Mulliken analyses, see ref 55–57.

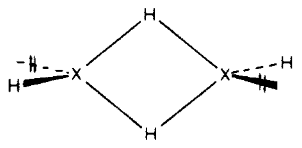
(55) Pēlissier, M.; Malrieu, J. P.; Serafini, A.; Labarre, J. F. *Theor. Chim. Acta* **1980**, *56*, 175.

(56) Lappert, M. C.; Pedley, J. B.; Sharp, G. J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 539.

(57) Mason, R.; Mingos, D. M. P. *J. Organomet. Chem.* **1973**, *50*, 53.

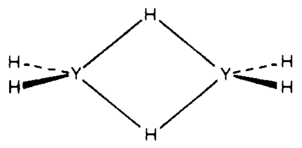
(58) Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568.

(59) The last reported parent compound is digallane: Downs, A. J.; Goode, M. J.; Pulham, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 1936.



X= Si,Ge,Sn,Pb

14

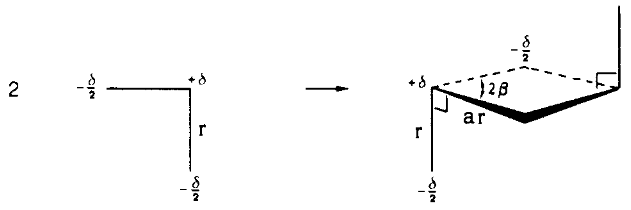


Y= B,Al,Ga

15

X–H–X bridge bond in X_2H_4. This charge enhancement is much less strong in X_2H_4 than in the fluoro derivatives[20] but is still significant. It also holds for the C^{-}–^{+}H polarity, which increases from CH_2 (–0.07/+0.03) to trans-bridged C_2H_4 (–0.10/+0.05).

The fairly constant binding energy of trans-bridged X_2H_4 with respect to two singlet XH_2 (Figure 4) may suggest further development of a simple electrostatic model. Reducing the problem to its extreme, let us imagine the coupling of two XH_2 species (XH = *r*; HXH = 90°; net charges = $+\delta$, $-\delta/2$) into a rhombus X_2H_4 (same HXH angles, same extracyclic XH distances, same net charges, intracyclic XH = *ar*, intracyclic HXH = 2β) as pictured in **16**. From the interaction energies of the point-charge distributions, the electrostatic energy of reaction **16** is expressed as



16

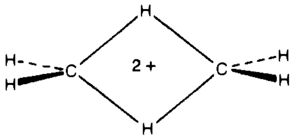
$$\Delta E = \frac{\delta^2}{r}\left\{-\frac{1}{2\sqrt{2}} - \frac{2}{a} + \frac{1}{\sqrt{1+a^2}} + \frac{1}{2a\cos\beta} + \frac{1}{8a\sin\beta} - \frac{1}{\sqrt{1+4a^2\cos^2\beta}} + \frac{1}{8\sqrt{1+a^2\cos^2\beta}}\right\} \quad (3)$$

Discarding the case of C_2H_4, *a* and β are fairly constant from Si_2H_4 to Pb_2H_4 ($a \simeq 1.1$; $2\beta \simeq 76°$). The binding energies therefore depend only on the δ^2/r ratio so that it should be constant to account for the constant wells in Figure 4. Simple electronegativities of the elements induce oscillations for the point charges from Si_2H_4 to Pb_2H_4, as calculated according to the Mulliken analyses. In turn this induces a nonconstant δ^2/r ratio along our series so that the model does not reproduce a constant binding energy. However, the order of magnitude and the variations of ΔE are satisfactorily reproduced by the model. The following energies were calculated with the above-mentioned values for *a* and β [in this case, relation 3 may be written as $\Delta E = -717\ (\delta^2/r)$, with ΔE in kilocalories per mole, δ and *r* in atomic units]:

		ΔE, kcal/mol	
	δ^2/r, au	model	full calculation
Si	0.059	-42	-31
Ge	0.032	-23	-27
Sn	0.062	-44	-33
Pb	0.051	-37	-29

We point out, lastly, that the optimal value of β that maximizes $|\Delta E|$ according to relation 3 corresponds to $2\beta \simeq 80°$, which is not far from the calculated H_1XH_1 values of Table IV. Remarkably, this value is not strongly dependent on *a* ($a = 1 \Rightarrow 2\beta = 78°$; $a = 1.2 \Rightarrow 2\beta = 81°$).

It is interesting to compare the geometry of the saddle point trans-bridged C_2H_4 with that of the doubly bridged ethane dication $C_2H_6^{2+}$, **17**, which is a true minimum (but not the absolute minimum) on the corresponding surface,[60,61] and which is *stricto sensu* isoelectronic with diborane. Since this species is the simple product of protonation of trans bridged C_2H_4 (**14**, X = C), both four-membered rings may be expected to have similar geometries. Actually, as calculated from 6-31G** SCF calculations,[60] the intra-ring CC distance is shorter in $C_2H_6^{2+}$ (1.54 Å) than in C_2H_4 (1.65 Å) and the angle on the carbon atom is therefore more open in $C_2H_6^{2+}$ (107°) than in C_2H_4 (97°). However, the two rings have rather similar geometries, as shown in **18**.



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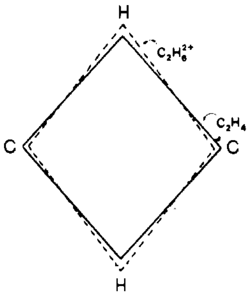

18

Conclusion

The large propensity for halogen bridges in the tin and lead compounds is well-documented.[62-66] We have shown through this study that bridged structures also exist as true minima in all group 14 X_2H_4 surfaces except for C_2H_4. The trans-bridged structures are even the absolute minima on the Sn_2H_4 and Pb_2H_4 surfaces. For the other surfaces, i.e., with C, Si, and Ge, the doubly bonded structures (planar for C_2H_4, trans bent for Si_2H_4 and Ge_2H_4) are the absolute minima. As predicted from simple rules previously proposed, the doubly bonded H_2 Pb=PbH$_2$ structure is not a real minimum. These rules also suggest that the heteropolar double-bond H_2Sn=PbH$_2$ may not exist as a true minimum.

Acknowledgment. I am grateful to Drs. J.-P. Malrieu and D. Liotard for constructive discussions and suggestions.

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(60) Olah, G. A.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 330.

(61) Schleyer, P. v. R.; Kos, A. J.; Pople, J. A.; Balaban, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3771.

(62) Abel, E. W. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., et al., Eds.; Pergamon Press: Oxford, U.K., 1973; Chapters 17 and 18, pp 43, 105.

(63) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: Oxford, U.K., 1983; Chapter 11, p 519.

(64) Harrison, P. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: Oxford, U.K., 1983; Chapter 12, p 629.

(65) Harrison, P. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: Oxford, U.K., 1987; Chapter 26, p 183.

(66) Hargittai, M. *Coord. Chem. Rev.* **1988**, *91*, 35.