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Theoretical Studies of Three-Membered Ring Compounds Y2H4X (Y = C, Si; X = CH2, NH, O, SiH2, PH, S)

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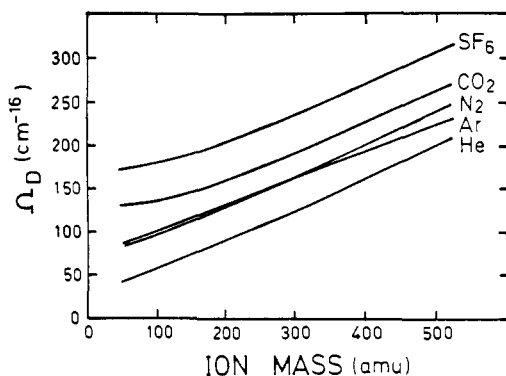**Figure 9.** Calculated collision cross section, Ω_D [$\times$ 10^{-16} cm], as a function of the ion mass, in helium, nitrogen, argon, CO_2, and SF_6.

section with ion mass are nearly independent of the type of drift gas and reflect mainly the increasing size of the ion. On the other hand, the relative values between light and heavy ions change considerably in the different drift gases. Thus, the cross section for the heaviest ion in helium is 5 times larger than that of the lightest ion; in CO_2, the ratio is above 2, while in SF_6 they differ by less than a factor of 2.

The results presented above reflect mainly the effect of the polarizability of the drift gas molecules on the mobility of ions. The high polarizability of SF_6 (about 20 times that of helium) results in a much stronger interaction and a larger collision cross section, which lead to a lower mobility, although the ion–neutral separation is slightly larger. This is also the reason why the mobility of a given ion in nitrogen, air, and argon is similar. The higher mass of argon, which gives a higher reduced mass, is counterbalanced by its slightly lower polarizability. In CO_2, on the other hand, the slight mass difference relative to argon and the much higher polarizability both lead to significantly lower reduced mobility values.

The mobility of heavy ions is less dependent on the nature of the drift gas than that of lighter ions. This is indicative of the weakening ion–neutral interaction as the ion size increases.

Summary

The mobility of the ions formed in an IMS cell from aliphatic and aromatic amines depends strongly on the properties of the drift gas molecules, especially on their polarizability and mass. The importance of the latter is reflected through the dependence of the reduced mass of the ion–neutral pair on the drift gas molecule's mass. The former is manifested through its effect on the collision cross section, by way of the interaction potential. The measured mobility values are reproduced quantitatively by the theoretical model for ions whose mass is no more than 2 or 3 times the mass of the drift gas molecules. However, once the m/M ratio increases above 3, the deviation between measured and calculated values also increases. Thus, in SF_6, for example, good agreement between the measured and calculated ion mobilities is obtained (except for the heaviest ion studied here). This also accounts for the success of this model with the hard-core potential to reproduce quantitatively most of the available experimental data, which generally dealt with ions of relatively low masses. However, the addition of the correction factor[1] to the interaction potential compensates for the sensitivity loss of the model to increments in the mass of heavy ions.

Thus, use of the corrected mobility formula in invaluable for predicting the mobility of ions over a broad mass range in a given drift gas. Furthermore, on the basis of this prediction, it is possible to select a suitable drift gas to obtain optimal separation of ions with similar mobilities.

Theoretical Studies of Three-Membered Ring Compounds Y_2H_4X (Y = C, Si; X = CH_2, NH, O, SiH_2, PH, S)

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The heats of formation of the three-membered ring compounds Y_2H_4X (Y = C, Si; X = CH_2, NH, O, SiH_2, PH, S) and the thermodynamics of the insertion reactions X + YH_2=YH_2 → c-Y_2H_4X are predicted by using MP2/6-31G(d) energies at the 6-31G(d) geometries. Bent bond lengths are calculated by tracing the path of maximum electron density connecting two nuclei, with the 6-31G(2d) basis set at the 6-31G(d) structures. The short Si–Si internuclear distances in Si_2H_4X (X = CH_2, NH, O, PH, S) apparently are the result of severe bond bending rather than significant π character in the Si–Si bonds.

I. Introduction

Experimental and theoretical studies of ring strain have largely been devoted to cyclic hydrocarbons[1-3] and heterocycles containing second-period atoms.[1,4-6]   Recent work on these systems has focused on the nature of ring binding,[7] analysis of inherent strain energies,[8] and substituent effects.[9] Several recent studies of cyclic compounds containing one or more third-period atoms,[5,10] particularly silicon,[11-13] have been published. These investigations

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include experimental structural determinations of small silicon-containing rings[5,14-21] and their associated chemistry,[22] as well as theoretical predictions of geometries,[13,23-27] vibrational frequencies and intensities,[25] and strain energies.[12a,23,26,27c] Still, much remains to be done in gaining a fundamental understanding of the bonding in small ring systems containing main-group metals.

The present work presents an analysis of the molecular structures and prediction of the heats of formation for the set of three-membered rings Y_2H_4X (Y = C, Si; X = CH_2, NH, O, SiH_2, PH, S). The relative energies of the reactants and products of the insertion reactions X + H_2Y=YH_2 → c-XY_2H_4 are also determined.

II. Computational Approach

Structures and force fields were computed at the Hartree–Fock SCF level, with the 6-31G(d) basis set.[28,29] This basis set includes a set of six d polarization functions on all heavy atoms. Second-order Møller–Plesset perturbation theory corrections[30] were made with this basis set (denoted MP2/6-31G(d)) in the determination of energetic quantities.

As an aid in the analysis of the molecular structures, "bent" bond lengths, defined as the path of maximum electron density (MED) connecting two atoms,[31] were computed. The MED path

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TABLE I: Bond Lengths and Mulliken π Overlap Populations[a]

molecule	bond	expt	L	λ	π overlap population
1a	C–C		1.497	1.507	0.031
2a	C–N		1.449	1.454	
	C–C		1.471	1.488	0.033
3a	C–O		1.401	1.404	
	C–C		1.453	1.474	0.036
4a	C–Si	1.826[b]	1.855	1.875	
		1.872[c]			
	C–C	1.520[b]	1.553	1.555	−0.046
		1.643[c]			
5a	C–P		1.853	1.874	
	C–C		1.492	1.497	−0.003
6a	C–S		1.811	1.826	
	C–C		1.473	1.480	0.025
1b	Si–C	1.886[d]	1.914	1.919	
		1.907[e,*]			
	Si–Si	2.272[d]	2.258	2.336	0.051
		2.327[e]			
2b	Si–N		1.736	1.740	
	Si–Si		2.238	2.353	0.056
3b	Si–O	1.694[f]	1.694	1.694	
	Si–Si	2.227[f]	2.200	2.332	0.058
4b	Si–Si	2.428[g,*]	2.350	2.378	0.009
		2.416[g,*]			
		2.407[h,*]			
		2.380[i,*]			
		2.402[i,*]			
		2.511[j]			
5b	Si–P		2.291	2.304	
	Si–Si		2.282	2.323	0.048
6b	Si–S	2.162[k]	2.163	2.168	
	Si–Si	2.289[k]	2.260	2.314	0.007
H_2C=CH_2					0.280
H_2Si=SiH_2					0.285

[a] All bond lengths in angstroms. L and λ denote the internuclear distance and bend bond length, respectively. The π overlap populations are determined at the 6-31G(2d)//6-31G(d) level. Asterisks indicate average bond length. [b] Reference 5. [c] Reference 18. [d] Reference 19. [e] Reference 20. [f] Reference 21a. [g] Reference 16. [h] Reference 17. [i] Reference 15. [j] Reference 14. [k] Reference 21b.

was determined for the Si–Si bond in disilaoxirane (**3b**) for several basis sets. Since spurious minima were found on the MED path unless two sets of d functions were used, all bent bond lengths reported here were obtained with the 6-31G(2d) basis set.[32] Reoptimization of the disilaoxirane geometry with the 6-31G(2d) basis set produces very small changes (less than 0.015 Å and 0.5° in bond lengths and bond angles, respectively) to that obtained at the 6-31G(d) level, so it is concluded that the smaller basis is reliable for geometry predictions.

Disch et al.[35] have demonstrated that homodesmic reactions[33] can be used to predict heats of formation of strained rings to within a few kcal/mol of experimental values. Such reactions have been used in this laboratory to predict heats of formation for cyclic and acyclic alkylsilanes.[34] In the present work the following homodesmic reactions are used:
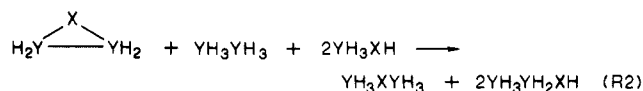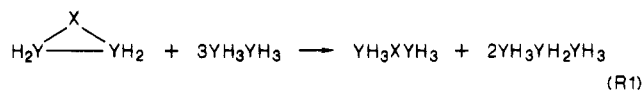
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$$H_2Y\overset{X}{\underset{\triangle}{\qquad}}YH_2 \ + \ 3YH_3YH_3 \ \longrightarrow \ YH_3XYH_3 \ + \ 2YH_3YH_2YH_3$$

(R1)

$$H_2Y\overset{X}{\underset{\triangle}{\qquad}}YH_2 \ + \ YH_3YH_3 \ + \ 2YH_3XH \ \longrightarrow$$

$$YH_3XYH_3 \ + \ 2YH_3YH_2XH \quad (R2)$$

MP2/6-31G(d) homodesmic reaction energies have been converted to $\Delta H_{r,0}$ for each reaction by including zero-point vibrational energy (ZPE) corrections, obtained from the computed harmonic frequencies (scaled by a factor of 0.89[36]). Then, by use of the known experimental heats of formation[34,37] of the acyclic species in (R1) and (R2), the calculated heats of reaction are used to predict heats of formation of the strained rings. Where necessary, conversion of the experimental heats of formation from 298 to 0 K has been done by using a method described previously.[38] The same homodesmic reactions are used to estimate strain energies.[39]

For the rings containing two silicon atoms, the experimental heats of formation of the SiH_3XSiH_3 and SiH_3SiH_2XH reference compounds in (R1) and (R2) are generally not known. These heats of formation must be estimated in the same way as described above. For example, the heat of formation of $SiH_3CH_2SiH_3$ can be computed from the reaction

$$SiH_3CH_2SiH_3 \ + \ CH_3CH_2CH_3 \ \rightarrow \ 2SiH_3CH_2CH_3 \quad (R3)$$

(Because of this extra step, one anticipates slightly larger errors in the predicted heats of formation for the corresponding cyclic compound.) Since no experimental heats of formation of silane derivatives Si_nH_mX ($n = 1, 2$) are known (except X = CH_2), predictions of the heats of formation of **2b**, **3b**, **5b**, and **6b** by this method are precluded. Previous calculations from this laboratory[34] have shown the experimental heat of formation of ethylsilane[37c] to be in substantial error. Consequently, we have used homodesmic reaction (R4) to estimate this quantity.

$$SiH_3CH_2CH_3 \ + \ CH_3CH_3 \ \rightarrow \ SiH_3CH_3 \ + \ CH_3CH_2CH_3 \quad (R4)$$
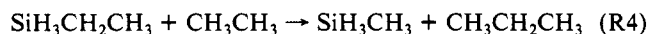
The predicted heat of formation of ethylsilane is -3.6 kcal/mol, in excellent agreement with our earlier estimate[34] of -4 kcal/mol.

All structures, energies, and vibrational frequencies were determined by using the analytical gradient methods in GAUSSIAN82.[40] The bent bond lengths were obtained with AIMPAC.[41]

III. Results and Discussion

The numbering scheme for the molecules of interest is summarized in Figure 1. All structures were fully optimized, within the confines of the symmetries indicated in the figure. The 6-31G(d) geometries are given in Figure 1, as are the experimental structures for **1a**,[42] **2a**,[43] **3a**,[44] **5a**,[45] and **6a**.[44] Partial comparisons

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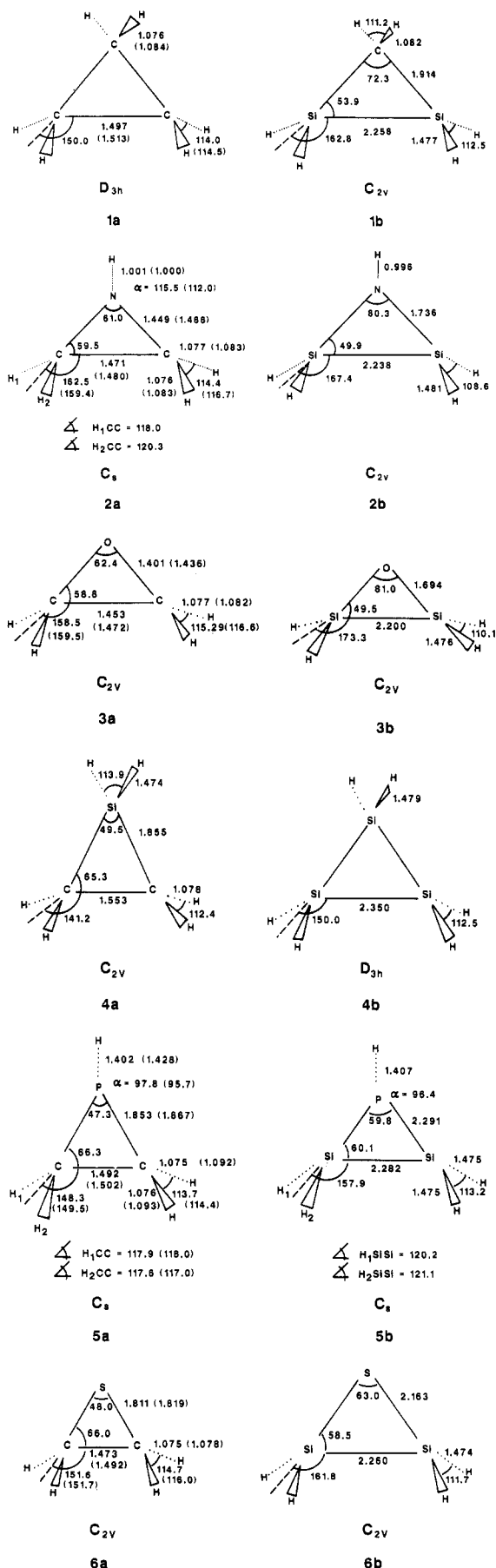
Figure 1. Bond lengths in angstroms and bond angles in degrees. α denotes the angle between the X–H bond and the plane containing the three heavy atoms. The dashed line is defined by the intersection of the plane containing the three heavy atoms and the plane containing YH_2. The symmetry of the molecule is located beneath its structure.

TABLE II: Heats of Formation ($\Delta H_{f,0}$) and Thermodynamics of Insertion Reactions for Three-Membered Rings[a]

molecule	$\Delta H_{f,0}$[b] SCF	MP2	obsd	insertion reaction[c] ΔE	$\Delta H_{r,0}$
1a	16.6	18.0	16.6	-121.7	-113.6 (-100.8)
	(16.6)	(18.0)	16.6		
2a	33.9	34.2	34.1	-115.0	-107.8 (-109.7)
	(35.6)	(36.6)	34.1		
3a	-8.6	-9.6	-9.7	-135.9	-131.7 (-128.7)
	(-8.4)	(-9.6)	-9.7		
4a	36.0	33.8		-48.7	-44.8
	(35.7)	(33.8)			
5a				-76.6	-72.3
6a	21.6	20.8	22.4	-88.8	-86.2 (-84.3)
	(20.1)	(20.2)	22.4		
1b	49.1	47.4		-136.7	-130.0
	(49.9)	(47.3)			
2b				-161.9	-155.6
3b				-200.9	-196.8
4b	70.2	68.3		-73.4	-69.2
	(70.2)	(68.3)			
5b				-105.2	-101.1
6b				-139.6	-136.6

[a] All values are in kcal/mol. [b] Computed heats of formation determined at the SCF (HF/6-31G(d)//HF(6-31G(d)) and MP2 (MP2/6-31G(d)//HF/6-31G(d)) levels. The observed values are obtained from experimental heats of formation (ref 41). The theoretical values (not) enclosed in parentheses are obtained by using homodesmic reaction R2 (R1). [c] Computed insertion energies and enthalpies determined at the MP2/6-31G(d)//HF/6-31G(d) level (see (R5) in text). The experimental values (determined from heats of formation, see ref 37) are given in parentheses. The experimental singlet–triplet energy splittings of CH_2, NH, O, PH, and S are taken from ref 49.

with experimental structures are made in Table I for compounds **4a, 1b, 3b, 4b,** and **6b**.

The agreement between the experimental and our calculated geometries for the compounds in Figure 1 is very good. The predicted C–C bond lengths are less than the experimental values by about 0.02 Å. The computed C–X bond lengths are shorter than experiment, the largest difference (0.04 Å) occurring in **2a**. The calculated C–H and X–H bond lengths are all within 0.03 Å of experiment, again generally less than the measured values. Inclusion of correlation corrections would increase the predicted bond lengths.[46] The experimental and theoretical H–C–H and H–X–(ring plane) bond angles agree to within 2° and 3°, respectively.

Experimental structures for the remaining compounds are not known. For molecules **4a, 1b, 3b, 4b,** and **6b**, the predicted structures may be *qualitatively* compared with experimental geometries of substituted analogues (Table I).

Recent studies by Grev and Schaefer[25a] and Cremer et al.[26] of **1b–6b** predicted structures that are nearly identical to ours: bond lengths and angles agree to within 0.02 Å and 3°, respectively. Pseudopotential calculations by Rubio and Illas[24] yielded Si–Si bond lengths of 2.331 and 2.381 Å for **4b** using effective double-ζ (DZ) and double-ζ plus polarization (DZP) basis sets, respectively. A 4-31G calculation[23] predicts a Si–Si bond length of 2.334 Å for **4b**. Previous calculated geometries of **4a** gave Si–C and C–C bond lengths of 1.892 and 1.563 Å (3-21G)[12] and 1.848 and 1.588 Å (3-21G*).[34a] A CNDO/2 investigation predicted Si–C (C–C) bond lengths of 1.891 (1.509) Å.[13]

Among the more interesting structural features are the unusually short Si–Si bond lengths in rings **1b–3b, 5b,** and **6b**: The calculated Si–Si bond lengths of **2b** and **3b** are actually closer to the double bond length in disilene (2.13 Å[47]) than to the Si–Si single bond length in disilane (2.36 Å[47]). Furthermore, the SiH₂

(46) Hehre, W. J.; Random, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Methods,* Wiley: New York, 1986.

(47) RHF/6-31G(d) C–X, Si–X single bond lengths and C–C, Si–Si double bond lengths (in angstroms): H_3C–CH_3 (1.527), H_3C–NH_2 (1.453), H_3C–OH (1.400), H_3C–SiH_3 (1.890), H_3C–PH_2 (1.860), H_3C–SH (1.818), H_3Si–NH_2 (1.729), H_3Si–OH (1.653), H_3Si–SiH_3 (2.361), H_3Si–PH_2 (2.272), H_3Si–SH (2.156), H_2C=CH_2 (1.317), H_2Si=SiH_2 (2.134).

TABLE III: Strain Energies and Enthalpies for Three-Membered Rings[a]

molecule	$-\Delta E$ SCF		MP2		$-\Delta H_{r,0}$ SCF	MP2	obsd
1a	28.8		30.2		25.9	27.3	26.0
	(28.8)	(28.0)[b]	(30.2)	(29.7)[b]	(25.9)	(27.3)	26.0
2a	25.9		26.3		22.9	23.2	23.1
	(29.6)	(29.8)[b]	(30.5)	(29.5)[b]	(26.7)	(27.7)	25.2
3a	24.1		23.1		20.9	19.9	19.8
	(30.9)	(31.6)[b]	(29.7)	(30.0)[b]	(27.8)	(26.6)	26.5
4a	45.1		42.9		43.1	40.9	
	(39.8)		(37.9)		(37.6)	(35.7)	
5a	24.4		22.0		22.4	20.0	
	(22.6)		(21.5)		(20.5)	(19.4)	
6a	18.5		17.7		16.3	15.5	17.1
	(19.2)		(19.3)		(16.9)	(17.0)	19.2
1b	46.3	46.3[c]	44.6	45.0[c]	44.3	42.6	
	(43.1)	(42.7)[c]	(40.5)	(40.5)[c]	(41.2)	(38.6)	
2b	48.8	49.2[c]	46.1	46.7[c]	47.2	44.5	
	(43.3)	(43.0)[c]	(39.7)	(39.5)[c]	(42.1)	(38.6)	
3b	58.0	59.2[c]	52.4	53.9[c]	56.4	50.8	
	(54.1)	(54.7)[c]	(46.7)	(47.7)[c]	(52.6)	(45.3)	
4b	39.0	38.9[c]	37.1	37.3[c]	37.5	35.6	
	(39.0)	(38.9)[c]	(37.1)	(37.3)[c]	(37.5)	(35.6)	
5b	32.3	32.2[c]	29.9	30.2[c]	30.8	28.4	
	(31.3)	(31.3)[c]	(29.2)	(29.5)[c]	(29.9)	(27.8)	
6b	30.2	30.5[c]	28.0	28.5[c]	28.9	26.7	
	(28.0)	(28.1)[c]	(25.2)	(26.9)[c]	(26.9)	(24.1)	

[a] All values are in kcal/mol. Computed values determined at the SCF (HF/6-31G(d)//HF/6-31G(d)) and MP2 (MP2/6-31G(d)//HF/6-31G(d)) levels. The observed values are obtained from experimental heats of formation (ref 41). The theoretical values (not) enclosed in parentheses are obtained by using homodesmic reaction R2 (R1). [b] From ref 7. [c] From ref 26.

groups in **3b** are nearly coplanar with respect to the Si–Si base bond. (The angle between the H–Si–H bisector and the Si–Si bond is 173.3°.) A similar, albeit attenuated, shortening of the base bond is found **2a, 3a,** and **6a**. This observation has been interpreted in terms of partial Si–Si π-bond character in **1b–3b, 5b,** and **6b**.[25a] However, the bent bond lengths all fall within the range 2.31–2.38 Å (Table I). This suggests that these are still really single bonds. To further probe the electronic structure of the Si–Si bonds, the Mulliken (6-31G(2d)) π overlap populations have been computed (Table I). The overlap populations are very small relative to those for ethylene and disilene and therefore may be of questionable significance.

Tables II and III summarize the SCF and MP2 heats of formation and strain energies, respectively, of **1a–6b**. As expected for homodesmic reactions, the effect of correlation on these quantities is minimal. With the exception of **3b**, where the difference in the SCF and MP2 strain energies is about 7 kcal/mol, the SCF and MP2 quantities agree to within about 2 kcal/mol.

The agreement between the experimental and theoretical strain energies and heats of formation is excellent, with the computed values consistently within 2 kcal/mol of experiment. This lends confidence to the computed heats of formation for silacyclopropane (**4a**), disilacyclopropane (**1b**), and cyclotrisilane (**4b**) (36.4, 47.4, and 68.3 kcal/mol, respectively), as well as to the calculated strain energies of **4a, 5a,** and **1b–6b**. Cremer and co-workers[7,26] have calculated the strain energies of **1a–3a** and **1b–6b** using homodesmic reactions and MP2/6-31G(d) energies without ZPE corrections. Their computed strain energies agree to within 1 kcal/mol of our values (Table III). The SCF/DZ strain enthalpy of **4b** computed by Grev and Schaefer[25b] using (R2) (36.7 kcal/mol) agrees very well with our SCF value of 37.5 kcal/mol. Sax and Kalcher[27c] have computed a similar value for this compound. Schoeller and Dabisch[23] have also computed the SCF/

(48) A bond critical point in the total electron density occurs wherever the gradient of the density is zero and two of the three curvatures are negative. See ref 31.

(49) Gordon, M. S.; Boatz, J. A.; Gano, D. G.; Friederichs, M. G. *J. Am. Chem. Soc.* **1987,** *109,* 1323–1325.

DZP strain energy of **4b**, using isodesmic reactions (without ZPE corrections). Their value of 31 kcal/mol is somewhat lower than our SCF strain energy of 39.0 kcal/mol.

(R1) and (R2) predict virtually identical heats of formation, the largest (MP2) difference (2.4 kcal/mol) occurring for **2a**. The agreement between the respective strain energies is less good. Except for compounds **1a** and **4b** (for which reactions R1 and R2 are identical), the RMS deviation in strain energies between the two sets of reactions is approximately 4 kcal/mol.

The energy and enthalpy differences for the insertions (R5)

$$H_2Y{=}YH_2 \ + \ X \ \longrightarrow \ H_2Y\underset{\displaystyle}{\overset{\displaystyle X}{\diagup\diagdown}}YH_2 \qquad \text{(R5)}$$
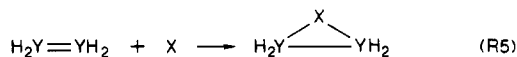
are found in Table II. These are computed with $(\Delta H_{r,0})$ and without (ΔE) ZPE corrections. The lowest singlet potential energy surfaces were assumed in determining these values. Except for cyclopropane (**1a**), the calculated values agree to within 3 kcal/mol of the experimental data. The reason for part of the 13 kcal/mol discrepancy for cyclopropane is that, at the MP2/6-31G(d)//6-31G(d) level of theory, the singlet–triplet energy splitting of CH_2 is predicted to be 21 kcal/mol, approximately 12 kcal/mol higher than experiment.[50a] If the computed singlet–triplet splitting in CH_2 were correct, the predicted ΔE and $\Delta H_{r,0}$ would be -109.7 and -101.6 kcal/mol, respectively. The latter value is in excellent agreement with the experimental value of -100.8 kcal/mol. A similar correction for the $CH_2 + H_2Si{=}SiH_2$ reaction gives ΔE and $\Delta H_{r,0}$ values of -124.7 and -118.0 kcal/mol, respectively.

The formation of each silicon-based ring is more exothermic than the formation of its corresponding carbon-based system. The reactions leading to the formation of **1a–3a** and **1b–3b** are the most exothermic, while those for **4a–6a** and **4b–6b** are less so. The least exothermic reaction is the one leading to silacyclopropane (**4a**); the most exothermic gives **3b**. With the adjusted values of -109.7 and -101.6 kcal/mol for $\Delta E_{r,0}$, and $\Delta H_{r,0}$, respectively, for the first reaction in Table II, it is evident that as the electronegativity of X increases for X in a given period, the corresponding insertion reaction becomes more exothermic.

These observations are likely due to three main effects: (1) the relative strengths of the C–C and Si–Si π bonds, (2) the relative strengths of the forming X–Y bonds, and (3) the relative strain energies of the forming three-membered rings. The fact that each silicon-based compound (**1b–6b**) has a larger exothermicity than its corresponding carbon-based ring (**1a–6a**) can be attributed to the weakness of the Si–Si π bond relative to the C–C π bond.[51] Less energy is expended in breaking the Si–Si π bond

than in breaking the C–C π bond, resulting in greater exothermicities for the formation of the silicon-based rings. The large exothermicities for **1a–3a** and **1b–3b** are due to the greater strength of the forming C–X and Si–X bonds for X = C, N, and O compared to X = Si, P, and S. The formation of **4a** is the least exothermic reaction since a C–C π bond must be ruptured in the process, and the ring strain of the product **4a** is the largest of the carbon-based rings **1a–6a**. Despite the fact that the ring strain of **3b** is the largest of all the rings **1a–6b**, the formation of **3b** is the most exothermic insertion reaction because of the relative ease of breaking the Si–Si π bond and the overwhelming stability of the highly ionic Si–O bonds.

IV. Conclusions

The major conclusions to be gleaned from this work are the following:

1. The Si–Si bonds in the silicon rings **1b–6b** are more bent than the C–C bonds of **1a–6a**. The displacement of the MED path away from the Si–Si internuclear axis can be as large as 0.3 Å, and the differences between the bent bond lengths and the corresponding internuclear Si–Si distances approach 0.15 Å.

2. The short Si–Si internuclear distances in **1b–3b**, **5b**, and **6b** appear to be a consequence of severe bond bending, rather than the result of significant π character in the Si–Si bond.

3. The three-membered silicon rings **1b–6b** generally have higher strain energies than their carbon counterparts **1a–6a**. Strain energies and heats of formation predicted by using homodesmic reactions are in good agreement with the available experimental data.

4. Multiple sets of polarization functions are required in heavy-atom basis sets in order to obtain meaningful electron density distributions of highly strained compounds containing third-row atoms.

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(51) (a) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217–5227. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.