not synchronous,[7] involves one of the hydrogen atoms originally bonded to the nitrogen moving quite close to the carbon atom before departing with another hydrogen atom from the carbon atom in the form of $H_2$. The important caveat emphasized by this study is that ab initio calculations at the 6-31G** level and semiempirical MNDO and MINDO/3 calculations are not necessarily reliable in their predictions as to the symmetries and geometries of cols on the potential energy surfaces of small organic cations. The case of $[CH_2NH_2]^+$ shows that consideration of correlation effects can be essential in mapping reaction pathways of small organic cations by means of molecular orbital calculations.

**Acknowledgment.** The financial support of the Australian Research Grants Scheme is gratefully acknowledged.

**Registry No.** $CH_3NH_2 \cdot HCl$, 593-51-1; $CD_3NH_2 \cdot HCl$, 7436-22-8; $CH_3ND_2 \cdot DCl$, 14779-55-6; $CD_3ND_2 \cdot DCl$, 14779-52-3; $[CH_2NH_2]^+$, 54088-53-8; $[CH_2ND_2]^+$, 111772-38-4; $[CD_2NH_2]^+$, 111772-39-5; $[CD_2ND_2]^+$, 111772-40-8; $[CH_2NHD]^+$, 111772-41-9; $[CD_2NHD]^+$, 111772-42-0; $[CH_3NH]^+$, 49784-84-1; $[CHNH]^+$, 38263-97-7; $[CNH_2]^+$, 86784-42-1; $[CH_2N]^+$, 53518-13-1; $D_2$, 7782-39-0.

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# Structure and Bonding in Cycloalkanes and Monosilacycloalkanes

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**Abstract:** The structural parameters and vibrational frequencies are predicted for the cycloalkanes $C_nH_{2n}$ and silacycloalkanes $SiC_{n-1}H_{2n}$, $n = 3$–6, using the 3-21G* basis set and SCF wave functions. Bent bond lengths are predicted by tracing the paths of maximum electron density connecting atomic centers. Strain energies and heats of formation are predicted for these compounds and some smaller acyclic alkylsilanes by using MP2/6-31G(d) energies at the 3-21G* geometries and the appropriate homodesmic reactions.

## I. Introduction

The concept of strain in small ring compounds has played an important role in chemistry since it was introduced more than a century ago. The nature of ring strain, its role in reactivity, and the importance of substituent effects have been the subject of several recent reviews.[1] The vast majority of attention, both experimentally and theoretically, has been devoted to cyclic compounds containing atoms in the first two periods of the periodic table, most particularly cyclopropane and cyclobutane and their derivatives.[2] Recently, however, several papers dealing with strain in cyclic molecules containing one or more silicon atoms in the ring have appeared in the literature.[2] Since the introduction of strained rings into a molecular environment can have a profound effect on the chemistry of the overall system, interest in strained cyclic compounds in which one or more carbons is replaced by a main group metal is likely to increase. Thus, it is important to develop a systematic understanding of how such substitutions affect molecular properties and chemical behavior.

This paper is the first in a series in which ab initio electronic structure theory is applied to investigations of small cyclic compounds with one or more carbon atoms replaced by a main group metal. In this first paper we examine the molecular structures, vibrational frequencies, and strain energies in the smallest cycloalkanes $C_nH_{2n}$ ($n$ = 3, 4, 5, 6) and their monosila analogues.

Also considered in this work are two important properties of strained ring compounds: bent bond lengths and heats of formation. The notion[3] that ring bonds are curved away from the bond axis has been explored in a quantitative manner recently by the groups of Bader[4,5] and Politzer.[6] These authors find that the bent bond distances can deviate significantly from the straight line distances connecting the two nuclei. One expects particularly large deviations in very highly strained systems. The heats of formation of the cycloalkanes are known experimentally, but the same is not the case for their silicon analogues. Thus, it is of interest to make use of theory to predict these values.

**Table I.** Homodesmic Reactions for Strained Rings

| | |
|---|---|
| $c\text{-}(CH_2)_3 + 3CH_3CH_3 \rightarrow 3CH_3CH_2CH_3$ | (R1) |
| $c\text{-}(CH_2)_4 + 3CH_3CH_3 \rightarrow n\text{-}C_4H_{10} + 2C_3H_8$ | (R2) |
| $c\text{-}(CH_2)_5 + 3CH_3CH_3 \rightarrow n\text{-}C_5H_{12} + 2C_3H_8$ | (R3) |
| $c\text{-}(CH_2)_6 + 3CH_3CH_3 \rightarrow n\text{-}C_6H_{14} + 2C_3H_8$ | (R4) |
| $c\text{-}(CH_2)_2SiH_2 + 3CH_3CH_3 \rightarrow CH_3SiH_2CH_3 + 2C_3H_8$ | (R5) |
| $c\text{-}(CH_2)_3SiH_2 + 3CH_3CH_3 \rightarrow CH_3SiH_2CH_2CH_3 + 2C_3H_8$ | (R6) |
| $c\text{-}(CH_2)_4SiH_2 + 3CH_3CH_3 \rightarrow CH_3CH_2SiH_2CH_2CH_3 + 2C_3H_8$ | (R7) |
| $c\text{-}(CH_2)_5SiH_2 + 3CH_3CH_3 \rightarrow CH_3SiH_2CH_2CH_2CH_2CH_3 + 2C_3H_8$ | (R8) |

In section II, the computational procedures used in this work are summarized. The calculated geometries and frequencies, strain

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(1) (a) Greenberg, A.; Liebman, J. F. *Chem. Rev.* **1976**, *76*, 311. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978. (c) Greenberg, A.; Stevenson, T. A. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 3, Chapter 5.

(2) (a) Tribble, M. T.; Allinger, N. L. *Tetrahedron* **1972**, *28*, 2147. (b) Oulette, R. J.; Baron, D.; Stolfo, J.; Rosenblum, A.; Weber, P. *Tetrahedron* **1972**, *28*, 2163. (c) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419. (d) Cartledge, R. K. *J. Organomet. Chem.* **1982**, *225*, 131. (e) Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1706. (f) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896.

(3) Coulson, C. A. *Valence*; Oxford: London, 1961.

(4) (a) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040. (b) Tal, Y.; Bader, R. F. W.; Erkku, J. *Phys. Rev. A* **1980**, *21*, 1. (c) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 631.

(5) (a) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. (b) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; McDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069. (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811.

(6) (a) Politzer, P.; Abrahmsen, L.; Sjoberg, P.; Laurence, P. R. *Chem. Phys. Lett.* **1983**, *102*, 74. (b) Politzer, P.; Domelsmith, L. N.; Abrahmsen, L. *J. Phys. Chem.* **1984**, *88*, 1752. (c) Politzer, P.; Jayasuriya, K.; Zilles, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 121.

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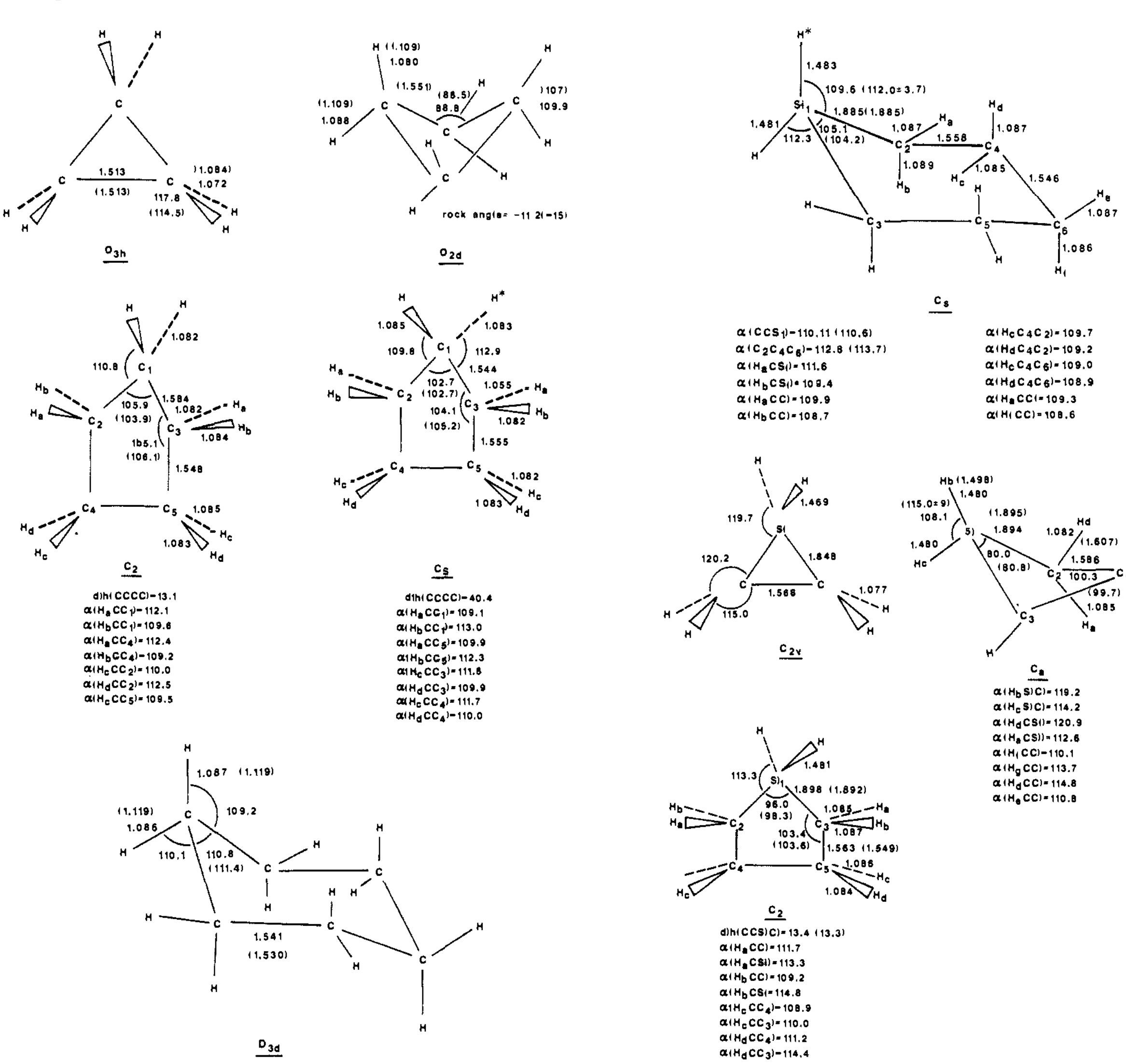

**Figure 1.** Molecular structures: bond lengths in angstroms, angles in degrees. Experimental values are given in parentheses: cyclopropane [Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1985**, *89*, 3298]; cyclobutane [Takabayashi, F.; Kambara, H.; Kuchitsu, K. 7th Austin Symposium on Gas Phase Molecular Structure, Austin, TX, paper WA6, March 1978]; cyclopentane [Adams, W. H.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013]; cyclohexane [Chiu, N. S.; Ewbank, J. D.; Schafer, L. *J. Mol. Struct.* **1982**, *86*, 397]; silacyclobutane [Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V.; Cyvin, B. N.; Cyvin, S. J. *Zh. Strukt. Khim.* **1975**, *16*, 473]; silacyclopentane and silacyclohexane [Shen, Q.; Hilderbrandt, R. L.; Mastryukov, V. S. *J. Mol. Struct.* **1979**, *54*, 121].

energies and heats of formation, and bent bond lengths are presented and discussed in section III. A general discussion of homodesmic and related reactions is given in section IV, resulting in the suggestion that the experimental heat of formation of ethylsilane and diethylsilane should be re-examined. The conclusions are presented in section V.

## II. Computational Methods

**A. Computational Levels.** Geometries and harmonic force fields (using the Schlegel algorithms[7] in GAUSSIAN82[8]) were obtained with the restricted Hartree–Fock (RHF) self-consistent-field (SCF) method,[9] using the 3-21G* basis set,[10] in which a set of five d functions is added only to the silicon 3-21G basis. For estimates of ring strain and heats of formation the larger 6-31G(d) basis set[11] was used at the 3-21G* geometries, at both the SCF and second-order many-body perturbation theory[12] levels. These are denoted SCF/6-31G(d)//3-21G* and MP2[13]/6-31G(d)//3-21G*, respectively.

**B. Homodesmic Reactions.** The strain energies have been evaluated with use of the appropriate homodesmic reaction.[14] Here, the strained molecule is compared, in a balanced chemical reaction, to a closely related unstrained analogue in a manner such that identifiable chemical groups are conserved in the reaction. This approach minimizes the contribution of correlation error to the computed energy differences, thereby making strain energies computed at the SCF level more reliable. The homodesmic reactions used for the eight molecules considered in the current work are summarized in Table I. Note, for example, in the cyclopropane reaction (R1) that the numbers of $CH_2$ and $CH_3$ groups are conserved. In general, the reactions listed in the table are not unique; however, it is our experience that alternative choices will give very similar results for strain energies. This is considered in more detail in section IV.

Disch and co-workers[15] have shown that these same homodesmic reactions may be used to predict heats of formation of strained rings to within a few kcal/mol of the experimental values. Following their approach, homodesmic reaction energies are calculated at the MP2/6-

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[7] Schlegel, H. B. *J. Comp. Chem.* **1982**, *3*, 215.

[8] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN82, Carnegie-Mellon University: Pittsburgh, PA, 1983.

[9] Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

[10] Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

[11] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1982**, *28*, 213. (b) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

[12] Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

[13] (a) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. (b) Pople, J. A.; Binkley, J. S.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

[14] (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. (c) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkins Trans. 2* **1977**, 1036.

[15] Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

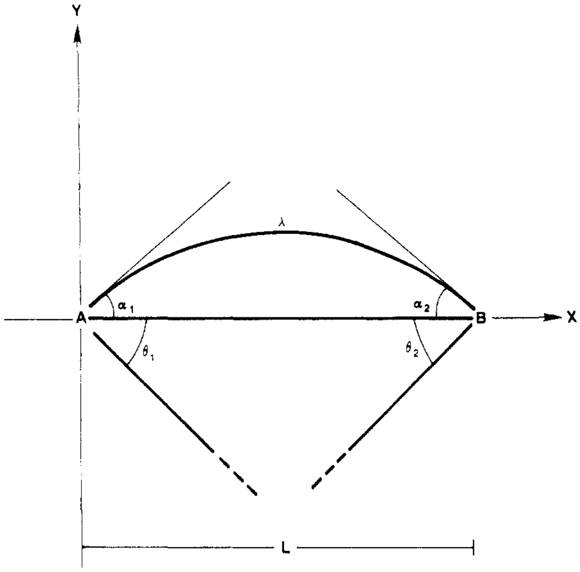

Figure 2. Definition of bent bond length parameters.

31G(d) level. The heat of the reaction at 0 K can then be obtained by adding the appropriate zero point vibrational energy corrections. For this purpose, rather than use vibrational frequencies obtained from a combination of experiment and molecular mechanics as suggested by Disch et al., we have chosen to use harmonic frequencies obtained from the 3-21G* calculations, corrected for an expected overestimation of the experimental values by introducing a multiplicative factor of 0.89.[16] The heat of the reaction calculated in this manner may then be combined with experimental heats of formation for the acyclic reference species in the reactions in Table I to obtain the heat of formation for the strained ring. Where necessary, conversion of the experimental heats of formation from 298 to 0 K may be accomplished in a manner described previously.[17]

For the silicon rings, the heats of formation are not known experimentally for all of the reference compounds. In these cases, an additional step is required in which the missing heat of formation is obtained in the same way as described above. For example, for diethylsilane one would write

$$\mathrm{CH_3CH_2SiH_2CH_2CH_3 + CH_3CH_2CH_3 \rightarrow CH_3SiH_2CH_3 + CH_3CH_2CH_2CH_2CH_3} \quad \text{(R9)}$$

since the experimental heats of formation of ethane, propane, and dimethylsilane have been measured. Because of this extra step, one expects the errors in the predicted heats of formation for the cyclic compounds considered in this way to be slightly larger than the others.

**C. Bent Bond Lengths.** To measure the curved bond path (bent bond length) of a strained bond A–B, we have explored two alternatives. First, we have followed the procedure introduced by Bader and co-workers,[4] in which the path of maximum total electron density is traced in three dimensions from nucleus A to nucleus B. The drawback to this method is that it depends on the availability of ab initio structures and energies, and this becomes increasingly difficult as the sizes of the molecules increase. Therefore, we have also developed the following approach, based simply on consideration of the molecular geometry, as illustrated in Figure 2.

We define $L$ to be the nucleus-to-nucleus distance, usually quoted as the bond length, $\lambda$ to be the curved bond length, and $\theta_0$ to be the ideal (tetrahedral) angle at both centers A and B. If $\theta_1$ and $\theta_2$ are the actual (observed) angles at centers A and B, respectively, then the initial slopes, $S_1$ and $S_2$, at these centers are given by

$$S_1 = \tan(\alpha_1) = \tan((\theta_0 - \theta_1)/2) \quad (1)$$

$$S_2 = -\tan(\alpha_2) = -\tan((\theta_0 - \theta_2)/2) \quad (2)$$

If we now assume that the slope changes linearly along the A–B ($x$) axis,

$$S_2 = S_1 - kL \quad (3)$$

then it follows (see Appendix I) that

$$\lambda = \frac{L}{2(S_1 + S_2)}\left\{S_1\sqrt{1 + S_1^2} + S_2\sqrt{1 + S_2^2} + \ln\left[\frac{\sqrt{1 + S_2^2} + S_2}{\sqrt{1 + S_1^2} - S_1}\right]\right\} \quad (4)$$

The curved bond lengths obtained from eq 4 may then be compared with those obtained from the ab initio calculations.

## III. Results and Discussion

**A. Structures and Vibrational Frequencies.** The 3-21G* predicted structures are compared with the experimental values in Figure 1. The predicted frequencies are compared with the experimental values (where the latter are available) in Tables SI–SVIII (supplementary material). At this level of theory, the agreement with experiment is generally good. Predicted bond lengths for the cycloalkanes are within 0.01 Å of the experimental values for CC bonds and 0.02 Å for CH bonds, while bond angles are predicted to within 2–3°. For cyclopentane, the structure was optimized in both $C_2$ and $C_s$ symmetries. The two structures, both of which are shown in Figure 1, have identical energies and one harmonic frequency that is essentially zero. The latter is consistent with a very small pseudorotation barrier.[18] When the molecule is restricted to a planar $C_{2v}$ structure, it optimizes to a $D_{5h}$ structure (not shown) which is 5 kcal/mol higher in energy than the puckered forms. The experimental parameters quoted in the figure are taken from Adams, Geise, and Bartell.[18] These authors also quote average CC and CH bond lengths of 1.546 and 1.1135 Å, respectively.

No experimental structure is available for unsubstituted silacyclopropane. The predicted structure for silacyclobutane (Figure 1) is in very good agreement with experiment, except for the somewhat long average CH bond length of 1.143 Å quoted by Mastryukov et al.[19] The average experimental CH bond lengths of 1.112 and 1.113 Å for silacyclopentane[20] and silacyclohexane,[21] respectively, are in better agreement with the calculated values, and the remaining structural parameters for these compounds are in good agreement as well. The average experimental CC bond length quoted for both molecules is 1.550 Å, while the average CCH angles are 110.1 and 110.5°, respectively.

Calculated and experimental[22] frequencies for a similar level of theory have been compared recently[23] for cyclopropane. The 4-31G results obtained by Dupuis and Pacansky[24] and Komornicki, Pauzat, and Ellinger[23] (KPE) are similar to those found here with 3-21G (see Table SI), as are the 6-31G(d,p) frequencies predicted by KPE. The 3-21G calculated frequencies for cyclobutane are compared with the experimental[25] values in Table SII. The descriptions given in the table for the normal modes are those suggested by Lord and Nakagawa.[26] (Of course, normal mode vibrations are generally combinations of several localized motions; therefore, assigned vibrational descriptions throughout this work are necessarily qualitative). Most of the calculated exocyclic vibrational frequencies are 10–15% too high. This is consistent with previous comparisons between theory and experiment.[16]

The calculated harmonic frequencies for both $C_s$ and $C_2$ cyclopentane are compared with the experimental values of Kruse and Scott[27] in Table SIII. In agreement with experiment, we find

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(16) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. J.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *S15*, 269.

(17) Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Phys. Chem.* **1985**, *89*, 2198.

(18) Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013.

(19) Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V.; Cyvin, B. N.; Cyvin, S. J. *J. Struct. Chem.* **1975**, *16*, 438.

(20) Durig, J. R.; Lafferty, W. J.; Kalasinsky, V. F. *J. Phys. Chem.* **1976**, *80*, 1199.

(21) Shen, Q.; Hilderbrandt, R. L.; Mastryukov, V. S. *J. Mol. Struct.* **1979**, *54*, 121.

(22) Duncan, J. L.; Burns, G. R. *J. Mol. Spectrosc.* **1969**, *30*, 253.

(23) Komornicki, A.; Pauzat, F.; Ellinger, Y. *J. Phys. Chem.* **1983**, *87*, 3847.

(24) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511.

(25) Aleksanyan, V. T.; Antipov, B. G. *J. Mol. Struct.* **1982**, *89*, 15.

(26) Lord, R. C.; Nakagawa, I. *J. Chem. Phys.* **1963**, *39*, 2951.

(27) Kruse, F. H.; Scott, D. W. *J. Mol. Spectrosc.* **1966**, *20*, 276.

**Table II.** Strain Energies (kcal/mol)[a]

| molecule | energy |  | enthalpy (0 K) |  |  |
|---|---|---|---|---|---|
|  | SCF | MP2 | SCF | MP2 | experiment[b] |
| cyclopropane | 28.8 | 30.3 | 25.8 | 27.3 | 25.8 |
| cyclobutane | 27.1 | 28.6 | 24.2 | 25.8 | 25.7 |
| cyclopentane | 6.7 | 7.8 | 4.9 | 6.1 | 5.3 |
| cyclohexane | 0.4 | 0.9 | −0.5 | −0.1 | −0.4 |
| silacycopropane | 45.2 | 43.4 | 43.2 | 41.4 |  |
| silacyclobutane | 26.4 | 26.6 | 24.6 | 24.7 | c |
| silacyclopentane | 6.1 | 5.8 | 4.8 | 4.5 |  |
| silacyclohexane | 4.9 | 4.7 | 4.2 | 4.0 |  |

[a] "Energy" refers to electronic energy differences; "enthalpy" differences are corrected for zero-point vibrational energies. [b] Experimental heats of formation for alkanes and cycloalkanes from: Cox, R. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 170; for methylsilane and dimethylsilane from: Pedley, J. B.; Iseard, B. S. *CATCH Tables for Silicon Compounds*; University of Sussex, 1972; for $Si_nH_{2n+2}$ and ethylsilane from: Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem., Ref. Data, Suppl.* **1982**, *11*, 2; diethylsilane from: Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analysed Thermochemical Data*, University of Ussex, 1977. [c] The strain energy in silacyclobutane has been estimated to be 24 kcal/mol, R. Walsh, private communication.

a vanishingly small frequency for the pseudorotational motion. The calculated frequencies are again generally 10% too high. Similar agreement is obtained for cyclohexane (Table SIV).

Since experimental frequencies are not available for silacyclopropane, the calculated values in Table SV have been scaled by a factor of 0.89 to provide an estimate of the expected experimental values. With two exceptions, the calculated frequencies for silacyclobutane are also found to be 10% too high (Table SVI). The exceptions are the a′ ring puckering and one of the a″ $CH_2$ twisting modes, for both of which the calculated frequency is actually lower than the experimental one. Similar comments apply to silacyclopentane (Table SVII). Although both the infrared[28] and Raman[29] spectra of silacyclohexane are known, the assignments of the vibrational frequencies are incomplete. A CCC bending frequency is assigned[28] to 450 $cm^{-1}$, whereas we find such a motion in the 384-, 697-, 824-, and 991-$cm^{-1}$ modes. $CH_2$ deformations have been assigned to frequencies of 797, 909, and 1006 $cm^{-1}$. These apparently correspond to the calculated values of 484, 880, and 998 $cm^{-1}$. Similarly, the experimental $SiH_2$ deformation frequencies of 863 and 946 $cm^{-1}$ probably correspond to the calculated values of 654 and 801 $cm^{-1}$. The assigned frequency for the $CH_2$ rock (908 $cm^{-1}$) apparently correlates with the calculated value of 1118 $cm^{-1}$. C–Si stretching frequencies are expected to be in the region 655–734 $cm^{-1}$. These appear to correlate with the calculated frequencies of 708 and 977 $cm^{-1}$ in Table SVIII.

**B. Strain Energies and Heats of Formation.** The strain energies calculated with the homodesmic reactions in Table I are summarized in Table II. For the cycloalkanes the experimental heats of formation needed to estimate the experimental strain energies are all available, and the calculated and experimental values are in excellent agreement. As one would expect for reactions of this type, the addition of correlation corrections has only a small effect on the calculated values. The predicted strain energy generally decreases as the size of the ring increases from 3 to 6 heavy atoms. For the cycloalkanes, the MP2/6-31G(d) strain enthapy/$CH_2$ group is 9.1, 6.5, 1.2, and 0.0 kcal/mol for the 3-, 4-, 5-, and 6-membered rings, respectively.

A similar trend is observed for the silacycloalkanes, but the decrease in strain from the 3- to the 4-membered ring is much more dramatic. Related to this is the observation that while silacyclopropane is considerably more strained than its hydrocarbon counterpart, the strain in the two 4-membered rings is almost the same. The latter is also observed experimentally and may be rationalized, at least in part, by inspection of the ring angles and relating them to the standard "unstrained" angles in the "unconstrained" species methylene and silylene. At the same level of theory as used for the rings, these angles are 105° and 93°, respectively.[30] This difference arises from the decreased ability of third period atoms to mix (hybridize) s and p functions due to the much larger difference in their sizes relative to the second period.[31]

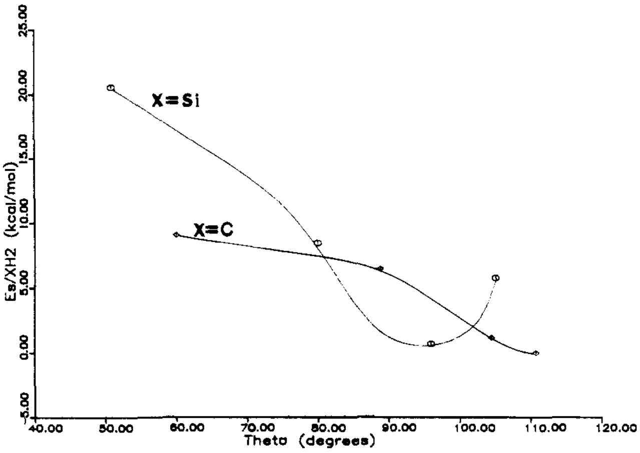

**Figure 3.** Strain energy $(E_s)/XH_2$ group as a function of bond angle: upper curve, X = Si; lower curve, X = C.

In cyclopropane, of course, the ring angles are all 60°, while in silacyclopropane the angles at silicon and carbon are 50° and 65°, respectively. Apparently, the very small angle at silicon gives rise to the very large strain in this compound, even though the deviation from the standard unstrained angle in cyclopropane (45°) is slightly larger than the deviations for the CCSi and CSiC angles in the silicon compound (40° and 43°, respectively). This suggests that the curve of strain vs angle rises sharply for very small angles, particularly for the silicon species. In cyclobutane, the ring angles are 89°, while in silacyclobutane, the CCC, CCSi, and CSiC angles are 100°, 90°, and 80°, respectively. Thus, the deviation from an unstrained angle in cyclobutane is 16° for all angles, while the deviations in silacyclobutane are only 5°, 15°, and 13° for the three angle types. Thus, because the normal angle for silicon is significantly smaller than that in carbon, the 4-membered silicon ring is better able to rearrange its structure to relieve the strain. This is illustrated further in tetrasilacyclobutane, where the ring angles are all 88°, and the computed strain is an even smaller 18 kcal/mol.[30b]

The foregoing argument is supported by the plots of strain versus angle in Figure 3. For the hydrocarbons, we simply plot the strain/$CH_2$ group as a function of the average CCC angle. For the silicon compounds, the strain in a $SiH_2$ group is estimated by assuming the $CH_2$ strain as a function of angle can be transferred to the silacycloalkanes. As suggested in the previous paragraph, the silicon curve is much steeper, although this curve actually rises slightly from silacyclopentane to silacyclohexane.

For hydrocarbons, Wiberg, Bader, and Lau[32] have argued that increased strain in a cyclic compound causes a shift in electron density from the hydrogens to the ring carbons. This is interpreted as stabilizing the carbons and destabilizing the hydrogens. Because there are more hydrogens than ring carbons, the net effect is destabilizing. The overall effect is smaller (per $CH_2$ group) as the strain decreases and is therefore smaller for cyclobutane than for cyclopropane. The presence of more $CH_2$ groups in the larger rings causes the net strain in the four-membered ring to be only slightly less than that in the three-membered ring. Now, elec-

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[28] Oshesky, G. D.; Bentley, F. F. *J. Am. Chem. Soc.* **1957**, *79*, 2057.

[29] Fogarasi, G.; Torok, F.; Vdovin, V. M. *Acta Chim. Acad. Sci. Hung. Tomus* **1967**, *54*, 277.

[30] (a) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421. (b) Gordon, M. S., unpublished results.

[31] For example, at the minimum basis set level, $\langle r \rangle$ = 1.592 and 1.688 bohr for carbon 2s and 2p orbitals, respectively, while $\langle r \rangle$ = 2.217 and 2.751 bohr for silicon 3s and 3p orbitals.

[32] Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

**Table III.** Calculated [6-31G(d)] and Experimental Heats of Formation (kcal/mol)

| molecule | SCF | MP2 | experiment[a] |
|---|---|---|---|
| cyclopropane | 16.8 | 18.3 | 16.8 |
| cyclobutane | 11.2 | 12.8 | 12.6 |
| cyclopentane | −11.4 | −10.3 | −11.1 |
| cyclohexane | −20.3 | −19.8 | −20.2 |
| silacyclopropane | 38.8 | 37.0 | |
| silacyclobutane | 20.0 | 19.0 | |
| silacyclopentane | −0.1 | −1.8 | |
| silacyclohexane | −6.8 | −9.1 | |

[a] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

tronegative substituents increase the strain in a ring compound. With regard to their study of polysilane rings, Grev and Schaefer[33] have noted that whereas hydrogens are electropositive substituents relative to carbon, they are electronegative relative to silicon. Thus, in addition to the geometric arguments given above, the relative electronegativity of silicon versus carbon (which decreases in importance as the size of the ring increases[33]) very likely increases the strain in silacyclopropane versus cyclopropane, while playing a smaller role in the relative strains in the two four-membered rings.

An alternative argument for the apparently anomalously small strain in cyclopropane is that there is some amount of stabilizing "$\sigma$ aromaticity" in this compound.[34-36] However, Grev and Schafer[33] have argued convincingly that this argument is based on the generally unsupportable assumption that parameters (e.g., force constants) derived from larger rings or unstrained reference compounds may be transferred to the smaller rings.

The homodesmic reactions used to estimate ring strain can also be used to predict the heats of formation of the eight compounds of interest. The results of these calculations are summarized in Table III. For the cycloalkanes, the experimental heats of formation are known for all reference compounds and for all four rings, so a direct comparison with theory is possible. As noted earlier by Disch and co-workers,[15] the agreement is excellent. The effect of perturbation theory on the theoretical predictions is small, ranging from a 0.1 to a 1.5 kcal/mol correction relative to the SCF results.

To our knowledge, none of the silacycloalkane heats of formation are known experimentally. Furthermore, the heats of formation for several of the larger alkylsilane reference species must also be estimated by using the following homodesmic reactions:

$$C_2H_5SiH_2C_2H_5 + CH_3CH_2CH_3 \rightarrow CH_3SiH_2CH_3 + C_2H_5CH_2C_2H_5 \quad \text{(R9)}$$

$$CH_3SiH_2(CH_2)_nCH_3 + CH_3CH_2CH_3 \rightarrow CH_3SiH_2CH_3 + CH_3(CH_2)_{n+1}CH_3 \quad (n = 1, 3) \quad \text{(R10)}$$

This procedure gives rise to predicted heats of formation of −16.2, −16.8, and −23.6 kcal/mol for 2-silabutane, 3-silapentane, and 2-silahexane, respectively, at the MP2/6-31G(d) level of computation. The corresponding SCF values are −16.1, −16.6, and −23.2 kcal/mol, respectively. It is expected that the necessity of calculating the heats of formation for these reference species will result in somewhat larger errors in the heats of formation predicted for the silacycloalkanes (Table III); however, these calculated values are still likely to be within 5 kcal/mol of experiment. (This is discussed in further detail in section IV below.) Note that, in analogy with the cycloalkanes, the heats of formation are predicted to decrease steadily as the ring strain decreases. Finally, it should be mentioned that semiempirical estimates of the heats of formation for silacyclopropane[37] and silacyclobutane[38] are 6.4 and −10.6 kcal/mol, respectively. Both values appear to be much too small.

**Table IV.** Comparison of Bent Bond Lengths and Internuclear Distances (Å)[a]

| | internuclear distance | | bent bond length | |
|---|---|---|---|---|
| molecule | experiment | theory | density | model |
| cyclopropane | 1.510 | 1.513 | 1.522 | 1.565 |
| cyclobutane | 1.548 | 1.569 | 1.571 | 1.578 |
| cyclopentane | 1.546 | 1.565 | 1.564 | 1.565 |
| | | 1.550 | 1.550 | 1.550 |
| | | 1.544 | 1.544 | 1.545 |
| cyclohexane | 1.536 | 1.542 | 1.542 | 1.542 |
| silacyclopropane | | | | |
| Si–C | | 1.848 | 1.868 | 1.923 |
| C–C | | 1.588 | 1.589 | 1.632 |
| silacyclobutane | | | | |
| Si–C | 1.895 | 1.894 | 1.902 | 1.912 |
| C–C | 1.600 | 1.586 | 1.587 | 1.594 |
| silacyclopentane | | | | |
| Si–C | 1.893 | 1.898 | 1.899 | 1.901 |
| C–C(a) | 1.550 | 1.563 | 1.563 | 1.564 |
| C–C(b) | 1.580 | 1.549 | 1.549 | 1.549 |
| silacyclohexane | | | | |
| Si–C | 1.885 | 1.885 | 1.885 | 1.885 |
| C–C(a) | 1.550 | 1.558 | 1.558 | 1.558 |
| C–C(b) | 1.550 | 1.546 | 1.546 | 1.546 |

[a] C–C(a) and C–C(b) refer to the carbon–carbon bonds adjacent to and one bond removed from the Si–C bond, respectively.

**Table V.** Heats of Formation (0 K) for $X_nH_{2n+2}$ Compounds (kcal/mol)[a]

| | X = C | | X = Si | |
|---|---|---|---|---|
| $n$ | experiment | theory | experiment | theory |
| 1 | −15.97 | −16.3 | 10.48 | 10.0 |
| 2 | −16.49 | −16.3 | 22.98 | 23.2 |
| 3 | −19.48 | −19.8 | 33.87 | 33.4 |

[a] See footnotes to Tables X and XI for experimental references.

C. **Bent Bond Lengths.** The predicted bent bond lengths are compared with the calculated and experimental internuclear distances in Table IV. Several general trends may be gleaned from this table: The difference between the calculated internuclear distance and the corresponding bent bond length decreases with the strain in the ring. For the 3- and 4-membered rings, the Si–C bonds are found to be more bent than the C–C bonds. The simple model presented in section II reproduces the trends in the total density bent bond lengths correctly, but generally it overestimates the degree to which these bonds are bent. The simplicity of the model is very appealing, however, and relaxation of some of its restrictions (for example, using an elliptical path, rather than a parabolic one) may lead to improved predictions of bent bond lengths.

## IV. Homodesmic Reactions

The accuracy of homodesmic reactions for predicting heats of formation at the MP2/6-31G(d) level of computation is an important consideration. This is particularly the case for the silicon compounds, due to the paucity of experimental data even for some of the necessary reference species. To probe this further, we have investigated several homodesmic and isodesmic (bond conserving, but not necessarily group conserving) reactions for several alkanes and alkylsilanes with known heats of formation.

Consider first the simple alkanes methane, ethane, and propane and their polysila analogues silane, disilane, and trisilane. One can write the following *iso*desmic reaction (X = C, Si)

$$2XH_3XH_3 \rightarrow XH_3XH_2XH_3 + XH_4 \quad \text{(R11)}$$

Since the experimental heats of formation of all species in (R11) are known, each heat of formation can be predicted by using the experimental value for the remaining compounds in the reaction

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(33) Grev, R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6569–6577.

(34) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957.

(35) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(36) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(37) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

(38) Dewar, M. J. S.; Low, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311.

**Table VI.** Heats of Formation (0 K) of Small Alkylsilanes (kcal/mol)[a]

| | | theory | | | |
|---|---|---|---|---|---|
| molecule | experiment | reaction R12 | reaction R13 | reaction R14 | reaction R15 |
| $CH_3CH_3$ | −16.49 | | | | 8.1 |
| $CH_3CH_2CH_3$ | −19.48 | | | | −44.1 |
| $SiH_4$ | 10.48 | 10.8 | | 6.2 | |
| $SiH_3CH_3$ | −3.96 | −4.3 | 0.7 | −1.8 | −28.6 |
| $SiH_3CH_2CH_3$ | −28.92 | | | | −4.3 |
| $CH_3SiH_2CH_3$ | −14.88 | −15.3 | −17.2 | −19.2 | |
| $(CH_3)_3SiH$ | −31.2 | −30.8 | −26.5 | | |

[a] See footnotes to Tables X and XI for experimental references.

and the MP2/6-31G(d) reaction enthalpy. The results of such calculations are summarized in Table V. The agreement between experiment and theory is uniformly excellent, with all errors being less than 0.5 kcal/mol.

Next consider the reactions

$$SiH_3CH_3 + (CH_3)_2SiH_2 \rightarrow (CH_3)_3SiH + SiH_4 \quad (R12)$$

$$SiH_3CH_3 + (CH_3)_3SiH \rightarrow 2(CH_3)_2SiH_2 \quad (R13)$$

$$2SiH_3CH_3 \rightarrow SiH_4 + (CH_3)_2SiH_2 \quad (R14)$$

$$SiH_3CH_3 + CH_3CH_2CH_3 \rightarrow SiH_3CH_2CH_3 + CH_3CH_3 \quad (R15)$$

Reactions R12–R14 are isodesmic reactions, while (R15) is homodesmic. Once again, the MP2/6-31G(d) heat of formation is predicted for each species with use of the experimental heats of formation for all other compounds in the reaction. The results are listed in Table VI. For reaction R12 the level of agreement with experiment is equivalent to that in Table V. This agreement deteriorates somewhat when reactions R13 and R14 are used. Still, the predicted heats of formation are within 5 kcal/mol of experiment, and one expects better agreement for the homodesmic reactions used in section IIIC. In view of this, the very poor agreement between experiment and theory when homodesmic reaction R15 is used is somewhat surprising and strongly suggests that the experimental heat of formation for ethylsilane is in error. It is likely that the 0 K value for this compound is −4 ± 5 kcal/mol. Similarly, the homodesmic reactions R9, R16, and R17 predict heats of formation of −16.8, −15.8, and −17.6 kcal/mol, respectively, for diethylsilane, rather than the experimentally reported value of −35.7 kcal/mol.

$$SiH_2(C_2H_5)_2 + 2CH_3CH_3 \rightarrow CH_3SiH_2CH_3 + 2CH_3CH_2CH_3 \quad (R16)$$

$$SiH_2(C_2H_5)_2 + 2CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_3 + 2n\text{-}C_4H_{10} \quad (R17)$$

We now turn to a consideration of alternative homodesmic reactions for the prediction of ring strain and heats of formation of the eight strained ring molecules. Reactions R1–R8 in Table I have been chosen for this purpose, since they allow a direct comparison of the strained ring with its unstrained analogue containing the same number of heavy atoms in the simplest possible manner. For the purpose of the present discussion these reactions will be referred to as set A. Three other sets (B, C, D) are listed in Table VII, along with the corresponding predicted MP2/6-31G(d) strain enthalpies and heats of formation.

The predicted heats of formation are quite insensitive to the specific choice of homodesmic reaction, the largest difference being 3.6 kcal/mol between sets C and D for the cyclobutanes. Similar comments apply to the predicted strain enthalpies for the cycloalkanes, with less than 2 kcal/mol deviation throughout. The strain enthalpies predicted for the silacycloalkanes exhibit somewhat greater deviations, particularly for sets B and C relative to sets A and D. The deviation of set C is not too surprising, since this is the only set of reactions in which the products do not contain an acyclic analogue of the strained ring of interest (this is the set used by Disch and co-workers). Set B is the only one that differs qualitatively from the others, since it predicts silacyclopentane to be less strained than silacyclohexane. Even so, with the exception of silacyclopentane, there is no strain energy that differs from that in set A by more than 3 kcal/mol.

**Table VII.** Alternative Homodesmic Reactions and MP2/6-31G(d) Enthalpies[a]

| reaction[b] | strain | formation |
|---|---|---|
| Set B | | |
| Cpr + 3Et → 3Pr | 27.3 (25.8) | 18.3 |
| Cbu + 2Et → 2Bu | 26.0 (26.8) | 11.9 |
| Cpe + Et + Pr → 2Pe | 6.5 (6.7) | −11.3 |
| Che + 2Pr → 2He | 0.6 (1.4) | −21.0 |
| Sicpr + 2Et + MeSi → Pr + EtSi + $Me_2Si$ | 38.8 | 37.0 |
| Sicbu + Et + MeSi → $SiH_3CH_2CH_2CH_3$ + $CH_3SiH_2CH_2CH_3$ | 22.7 | 18.1 |
| Sicpe + Et + $Me_2Si$ → $2CH_3CH_2SiH_2CH_2CH_3$ | −0.5 | −2.8 |
| Siche + Pr + EtSi → $SiH_3(CH_2)_4CH_3$ + $CH_3SiH_2(CH_2)_3CH_3$ | 5.3 | −10.2 |
| Set C | | |
| Cpr + 3Et → 3Pr | 27.3 (25.8) | 18.3 |
| Cbu + 4Et → 4Pr | 25.6 (24.6) | 13.7 |
| Cpe + 5Et → 5Pr | 5.6 (3.9) | −9.3 |
| Che + 6Et → 6Pr | −0.8 (−2.2) | −18.7 |
| Sicpr + 3Et → 2Pr + $Me_2Si$ | 41.4 | 37.0 |
| Sicbu + 4Et → 3Pr + $Me_2Si$ | 27.3 | 19.9 |
| Sicpe + 5Et → 4Pr + $Me_2Si$ | 9.5 | −0.8 |
| Siche + 6Et → 5Pr + $Me_2Si$ | 5.4 | −7.9 |
| Set D | | |
| Cpr + 3Et → 3Pr | 27.3 (25.8) | 18.3 |
| Cbu + 4Pr → 4Bu | 26.4 (28.9) | 10.1 |
| Cpe + 5Bu → 5Pe | 6.8 (5.5) | −9.8 |
| Che + 6Pe → 6He | 0.8 (0.3) | −19.7 |
| Sicpr + 3Et → 2Pr + $Me_2Si$ | 41.4 | 37.0 |
| Sicbu + 4Pr → 3Bu + $CH_3CH_2SiH_2CH_3$ | 25.3 | 16.3 |
| Sicpe + 5Bu → 4Pe + $CH_3CH_2SiH_2CH_2CH_3$ | 5.2 | −1.3 |
| Siche + 6Pe → 5He + $CH_3SiH_2(CH_2)_3CH_3$ | 4.8 | −7.8 |

[a] In kcal/mol, at 0 K. Experimental values are given in parentheses. [b] Et = ethane, Pr = propane, Bu = butane, Pe = pentane, He = hexane, Cpr = cyclopropane, Sicpr = silacyclopropane, MeSi = methylsilane, $Me_2Si$ = dimethylsilane, Cbu = cyclobutane, Sicbu = silacyclobutane, Cpe = cyclopentane, Sicpe = silacyclopentane, Che = cyclohexane, Siche = silacyclohexane, EtSi = ethylsilane.

## V. Conclusions

The following conclusions may be drawn from the work presented here:

(1) The curves of ring strain versus ring size ($n$) for cycloalkanes and silacycloalkanes cross at about $n = 4$. The rapid decrease in strain from silacyclopropane to silacyclobutane may be traced to the preference of silicon for angles near 90°. The strain energies, as measured by homodesmic reactions, are in good agreement with available experimental values.

(2) The path of maximum electron density (MED) is significantly larger than the internuclear distance for the three-membered rings. The two measures of bond length converge to a common value as the size of the ring increases and the ring strain decreases. The simple geometric formula follows the trends predicted by the MED paths, but it tends to overestimate the amount of curvature in the bonds of the small rings.

(3) Predicted heats of formation agree to within a few kcal/mol with the experimental values where they are known. On the basis of this agreement, we suggest that the experimental heats of formation of ethylsilane and diethylsilane have been underestimated by as much as 20 kcal/mol.

(4) The predicted strain energies and heats of formation appear to be rather insensitive to the choice of homodesmic reaction.

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**Appendix**

Consider an arc length $a$ joined by a segment of length $L$ as shown in Figure 2. The boundary conditions are

$$\left(\frac{dy}{dx}\right)_{x=0} = S_1, \quad \left(\frac{dy}{dx}\right)_{x=L} = -S_2 \qquad \text{(A1)}$$

In general, we assume the slope of the arc varies linearly, so

$$\frac{dy}{dx} = S_1 - kx \qquad \text{(A2)}$$

$$\left(\frac{dy}{dx}\right)_{x=L} = S_1 - kL = -S_2 \qquad \text{(A3)}$$

So,

$$k = \frac{S_1 + S_2}{L}; \quad \frac{dy}{dx} = S_1 - \frac{(S_1 + S_2)}{L}x \qquad \text{(A4)}$$

Now, by definition of arc length,

$$d\lambda = \left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2} dx$$

$$d\lambda = \left[1 + S_1^2 - \frac{2S_1(S_1 + S_2)}{L}x + \frac{(S_1 + S_2)^2x^2}{L^2}\right]^{1/2} dx$$

Integrating $d\lambda$ from 0 to $L$ and rearranging gives eq 4 in the text.

**Supplementary Material Available:** Tables of harmonic frequencies for cyclopropane, cyclobutane, cyclopentane, cyclohexane, silacyclopropane, silacyclobutane, silacyclopentane, and silacyclohexane (8 pages). Ordering information is given on any current masthead page.

# Band Electronic Structure of the Lithium Molybdenum Purple Bronze $Li_{0.9}Mo_6O_{17}$

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**Abstract:** The electronic structure of $Li_{0.9}Mo_6O_{17}$ was examined by performing tight-binding band calculations, and the calculated band electronic structure was analyzed in terms of orbital interaction analysis. $Li_{0.9}Mo_6O_{17}$ is three-dimensional in crystal structure but pseudo-one-dimensional (1D) in electrical properties, because the partially filled d-block bands of $Li_{0.9}Mo_6O_{17}$ originate primarily from the $Mo_4O_{18}$ chains embedded in the $Mo_4O_{15}$ octahedral layers. Of the four filled d-block bands of $Li_{0.9}Mo_6O_{17}$, two partially filled bands are dispersive along the $Mo_4O_{18}$ direction. Each of these two bands provides an identical 1D Fermi surface nested by the vector $\mathbf{q} \cong (0, 0.45b^*, 0)$. Therefore, it is likely that $Li_{0.9}Mo_6O_{17}$ is susceptible to either a charge or spin density wave formation associated with the nesting vector. The resistivity upturn at 25 K and the superconductivity at ~1.9 K in $Li_{0.9}Mo_6O_{17}$ were discussed on the basis of the calculated Fermi surfaces.

Molybdenum purple bronzes $A_{0.9}Mo_6O_{17}$ (A = K[2], Na[3]) and $TlMo_6O_{17}$[4] are two-dimensional (2D) metals and exhibit a charge density wave (CDW) phenomenon. $K_{0.9}Mo_6O_{17}$ consists of metal–oxygen layers of composition $Mo_6O_{17}$, constructed from $MoO_6$ octahedra and $MoO_4$ tetrahedra by sharing their oxygen corners, and the $K^+$ cations lie in between such $Mo_6O_{17}$ layers.[2a] This 2D character of the crystal structure gives rise to the 2D metallic properties of $K_{0.9}Mo_6O_{17}$. In structure and physical properties, $Na_{0.9}Mo_6O_{17}$[3] and $TlMo_6O_{17}$[4] are similar to $K_{0.9}Mo_6O_{17}$.[2] However, it is not the case with $Li_{0.9}Mo_6O_{17}$.[5] This lithium purple bronze has a three-dimensional (3D) crystal structure, but it exhibits pseudo-one-dimensional (1D) metallic character,[5] eventually becoming a superconductor at ~2 K.[5] Furthermore $(Li_{1-x}Na_x)_{0.9}Mo_6O_{17}$ (≤0.48) and $(Li_{1-x}K_x)_{0.9}Mo_6O_{17}$ ($x \leq 0.40$) exhibit superconductivity at ~2 K[5d,e] despite random potentials expected from the presence of mixed alkali cations. To gain some insight into these apparently puzzling structural and electrical properties of $Li_{0.9}Mo_6O_{17}$, we examine the electronic structure of $Li_{0.9}Mo_6O_{17}$ by performing tight-binding band calculations[6,7] based upon the extended-Hückel method.[8] The atomic

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(2) (a) Vincent, H.; Ghedira, M.; Marcus, J.; Mercier, J.; Schlenker, C. *J. Solid State Chem.* **1983**, *43*, 113. (b) Buder, R.; Devenyi, J.; Dumas, J.; Marcus, J.; Mercier, J.; Schlenker, C. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, L59. (c) Bervas, E.; Cochrane, R. W.; Dumas, J.; Escribe-Filippini, C.; Marcus, J.; Schlenker, C. *Lect. Notes Phys.* **1985**, *217*, 144. (d) Dumas, J.; Bervas, E.; Marcus, J.; Salomon, D.; Schlenker, C. *J. Mag. Magn. Mater.* **1983**, *31–34*, 535. (e) Escribe-Filippini, C.; Konate, K.; Marcus, J.; Schlenker, C.; Almairac, R.; Ayroles, R.; Roucau, R. *Philos. Mag. B* **1984**, *50*, 321.

(3) (a) Gatehouse, B. M.; Lloyd, D. J.; Miskin, B. K. *NBS Spec. Publ. (U.S.)* **1972**, *No. 364*, 15. (b) Stephenson, N. C. *Acta Crystallogr.* **1966**, *20*, 59. (c) Greenblatt, M.; Ramanujachary, K. V.; McCarroll, W. H.; Neifeld, R.; Waszczak, J. V. *J. Solid State Chem.* **1985**, *59*, 149.

(4) (a) Ganne, M.; Dion, M.; Boumaza, A.; Tournoux, M. *Solid State Commun.* **1986**, *59*, 137. (b) Ramanujachary, K. V.; Collins, B. T.; Greenblatt, M. *Solid State Commun.* **1986**, *59*, 647.

(5) (a) Onoda, M.; Toriumi, K.; Matsuda, Y.; Sato, M. *J. Solid State Chem.* **1987**, *66*, 163. (b) Schlenker, C.; Schwenk, H.; Escribe-Filippini, C.; Marcus, J. *Physica* **1985**, *135B*, 511. (c) Greenblatt, M.; McCarroll, W. H.; Neifeld, R.; Croft, M.; Waszczak, J. V. *Solid State Commun.* **1984**, *51*, 671. (d) Ramanujachary, K. V.; Collins, B. T.; Greenblatt, M.; McNally, P.; McCarroll, W. H. *Solid State Ionics* **1986**, *22*, 105. (e) Matsuda, Y.; Onoda, M.; Sato, M. *Physica* **1986**, *143B*, 243. (f) Sato, M.; Matsuda, Y.; Fukuyama, H. *J. Phys. C*, submitted for publication.

(6) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(7) Whangbo, M.-H.; Schneemeyer, L. F. *Inorg. Chem.* **1986**, *25*, 2424 and references cited therein for details of our tight binding calculations.

0002-7863/88/1510-0358$01.50/0