Anomaly in the Ring Strain Behaviour of Cyclopropane, Cyclobutane, and Cyclopentane, compared with their Silicon Analogues; a Theoretical Study

Wolfgang W. Schoeller and Thomas Dabisch

Fakultät für Chemie, Universität Bielefeld, Postfach 8640, 48 Bielefeld 1, Federal Republic of Germany

Cyclotrisilane and cyclopropane possess comparable ring strain while cyclotetrasilane is almost and cyclopentasilane and cyclopentane are entirely free of ring strain, indicating anomalous properties for cyclotetrasilane, which has less ring strain than cyclobutane.

As a general rule in organic chemistry the ring strain in cyclopropane (**1a**) is almost equal to that in cyclobutane (**2a**), while cyclopentane (**3a**) is free of strain.[1] On this basis, (**1a**) and (**2a**) have similar reactivity (*e.g.* towards electrophilic reagents). That the strain in (**1a**) and (**2a**) is almost equal has been attributed to σ-aromaticity[2] in the former. Here we reveal essential differences in bonding between the cyclosilanes[3] (**1b**)—(**3b**) and the corresponding cycloalkanes (**1a**)—(**3a**). We show that cyclotetrasilane (**2b**) is almost free of strain, in contrast to cyclobutane (**2a**).

The main differences in bonding between silanes and alkanes are as follows: (a) silicon is more electropositive than carbon, and thus Si–Si bonds have more s character than C–C bonds;[4] (b) silanes absorb light at longer wavelengths than alkanes,[5] indicating the presence of energetically low-lying unoccupied orbitals (narrow HOMO–LUMO splitting).

The most important bonding features of the cyclosilanes (cycloalkanes) (**1**)—(**3**) and their open congeners, silane (methane) and disilane (ethane), as obtained from *ab initio* SCF calculations at a double zeta level[6] are summarized in Table 1. The Si–Si equilibrium bond lengths in the cyclosilanes are almost equal to those in disilane.

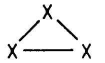
A quantitative estimate of ring strain in (**1**)—(**3**) is given by the energy balances obtained from the isodesmic reactions (1a) and (1b). Negative values refer to exothermic and positive values to endothermic reaction enthalpies (Table 1).

$$\text{cyc-C}_n\text{H}_{2n} + n\,\text{CH}_4 \longrightarrow n\,\text{C}_2\text{H}_6 + \Delta H \qquad (1a)$$

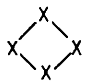
$$\text{cyc-Si}_n\text{H}_{2n} + n\,\text{SiH}_4 \longrightarrow n\,\text{Si}_2\text{H}_6 + \Delta H \qquad (1b)$$

Accordingly, the cycloalkanes (**1a**) and (**2a**) have almost equal ring strain, in agreement with conventional ring strain energies estimated from experiment.[1] In contrast, in the cyclosilane series, (**2b**) is almost strain-free as compared with (**1a**) or (**1b**). The five-membered rings (**3a**) and (**3b**) are slightly more stable than their open-chain congeners. Thus cyclotetrasilane (**2b**) has an exceptional position in these series of ring structures.†

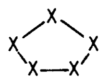
The gross atomic populations of the (banana-type) ring bonds (obtained from Boys localization[7] of the canonical orbitals) indicate more s character for the Si–Si bonds than for the C–C bonds, slightly larger in cyclotetrasilane (**2b**) ($sp^{1.68}$) than in (**3b**) ($sp^{1.73}$). In the cycloalkanes the s-content of the ring bonds increases from (**1a**) to (**3a**). Again this emphasizes the peculiarity of the four-membered ring in the cyclosilane series, yet the overall larger s content of the ring bonds for the silicon compounds parallels the trend for ethane and disilane.[4]



(**1**)



(**2**)



(**3**)

a; X = CH_2
b; X = SiH_2

Finally, the bonding picture of the ring systems will be completed by an inspection of the sets of (frontier) Walsh orbitals[8] for (**1a,b**) compared with those for (**2a,b**) (Figure 1). In all cases the replacement of carbon by silicon raises the orbital energies, owing to the more electropositive character of silicon. In addition, in (**2b**) compared with (**2a**), the order of Walsh orbitals is reversed: the degenerate e_u set [in (**2a**)] or the b_{1g} orbital [in (**2b**)] is the HOMO. The depression of the orbitals e_u below b_{1g} is caused by second order perturbation of the former by its antibonding counterpart of lowest energy and the same symmetry.‡ Since the antibonding e_u Walsh orbitals are constituted mainly from s atomic orbitals,[8] their admixture causes an increase of s content in the ring bonds. As a further consequence (**2b**) gains additional stability with respect to (**1b**) in agreement with the much lower ring strain in the former.

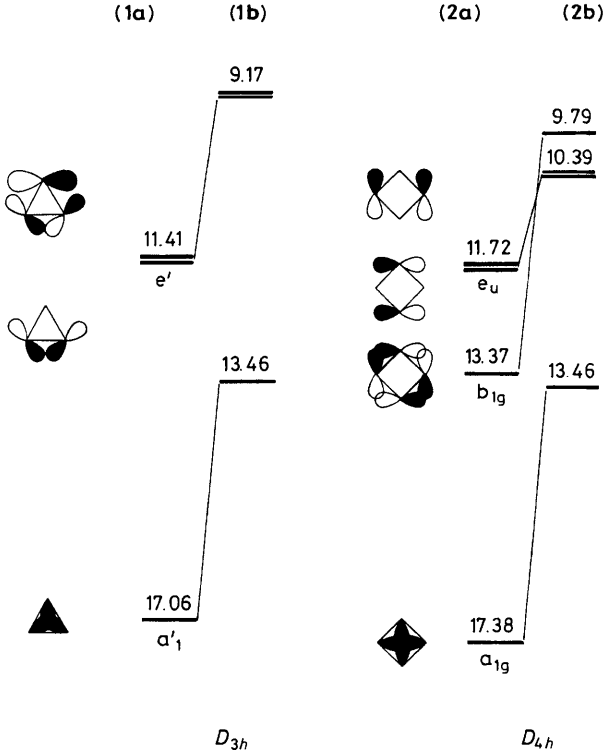


Figure 1. Energies ($-E$/eV) of the Walsh orbitals in (**1a,b**) and (**2a,b**) as obtained from the *ab initio* calculations at the double zeta level (ref. 6b).

---

† Homodesmic reactions parallel the trends of the isodesmic reactions but yield slightly larger overall reaction enthalpies.

‡ As can be shown in detail (unpublished results), such a perturbation is much weaker in (**1b**), because the e′ degenerate bonding set overlaps much less with its antibonding counterpart in the three-membered ring system; see also R. Hoffman and R. B. Davidson, *J. Am. Chem. Soc.*, 1971, **93**, 5699.

Table 1. Optimized geometries of (**1a,b**)—**3a,b**), silane (methane) and disilane (ethane), heats of reaction (in kcal/mol; 1 cal = 4.184 J), and separation of the localized orbitals of the ring bonds (Mulliken gross atomic populations). Numbers in parentheses are data for the carbon compounds.

		Bond length/Å		Bond angle/°		Gross atomic population		
Compound	Symmetry	SiSi (CC)	SiH (CH)	HSiH (HCH)	ΔH	s	p	d
cyc-X_3H_6	D_{3h}	2.334	1.494	112.4	−30.6	0.35	0.69	0.03
		(1.512)[a]	(1.083)	(114.0)	(−27.7)	(0.21)	(0.81)	(0.02)
cyc-X_4H_8	D_{4h}	2.371	1.497	107.9	−6.1	0.38	0.64	0.03
		(1.549)[b]	(1.084)	(108.0)	(−24.6)	(0.26)	(0.77)	(0.02)
cyc-X_5H_{10}	D_{5h}	2.380[c]	1.490	112.0	6.9	0.37	0.64	0.03
		(1.526)[c]	(1.088)	(109.6)	(7.0)	(0.26)	(0.75)	(0.02)
XH_4	T_d		1.489	109.5				
			(1.086)[a]	(109.5)				
X_2H_6	D_{3d}	2.353	1.448	108.3		0.39	0.62	0.03
		(1.526)[a]	(1.088)	(107.4)		(0.28)	(0.74)	(0.02)

[a] Bonding parameters (for the carbon compounds) taken from M. S. Gordon, *J. Am. Chem. Soc.*, 1980, **102**, 7419. [b] D. Cremer, *J. Am. Chem. Soc.*, 1977, **99**, 1307. [c] Assumed.

Our theoretical findings reveal that the bonding properties (ring strain, nature of frontier orbitals) in cyclotetrasilane (**2b**) are in variance with those in cyclobutane (**2a**), but not for the three-membered (and five-membered) ring systems. In a qualitative sense the outlined MO considerations should hold equally well for the higher congeners in the ring series X = GeH_2 and SnH_2.

The authors thank the Fonds der Chemischen Industrie and the Deutschen Forschungsgemeinschaft for support.

Received, 10th June 1985; Com. 796

References

1 S. W. Benson, 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976.

2 M. J. S. Dewar, *J. Am. Chem. Soc.*, 1984, **106**, 669; W. W. Schoeller, *Tetrahedron*, 1973, **29**, 929.

3 (a) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, *J. Am. Chem. Soc.*, 1982, **104**, 1150; A. Schäfer, M. Weidenbruch, K. Peters, and H. G. v. Schnering, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 302; S. Masamune, Y. Hanzawa, and D. J. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 6136; S. Masamune, L. R. Sita, and D. J. Williams, *ibid.*, 1983, **105**, 630; J. C. Dewan, S. Murakami, J. T. Snow, S. Collins, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 1985, 892; (b) R. West in 'Comprehensive Organometallic Chemistry,' vol. 2, eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, New York, 1982.

4 K. Kovačević, K. Krmpotić, and Z. B. Maksić, *Inorg. Chem.*, 1977, **16**, 1421.

5 Ref. 3(b), pp. 388—393.

6 (a) Energy optimizations of structures were performed at a STO-4/31 G level: L. C. Snyder and Z. Wasserman, *Chem. Phys. Lett.*, 1977, **51**, 349. (b) Energy balances were obtained utilizing the STO-4/31 G geometries with the following basis sets: C (8,4) in the contraction (4,4X1/2,2X1); Si (11,7) in the contraction (5,6X1/4,3X1); H (3,1) (S. Huzinaga, 'Approximate Atomic Functions. II,' Technical Report, The University of Alberta, Edmonton, Alberta, Canada, 1971) plus one set of polarization functions at C and Si; $\zeta_d(C) = 0.30$, $\zeta_d(Si) = 0.40$.

7 S. F. Boys in 'Quantum Theory of Atoms, Molecules and the Solid State,' ed. P.-O. Löwdin, Interscience, New York, 1967, p. 253.

8 M. Klessinger, 'Elektronenstruktur organischer Moleküle,' Verlag Chemie, Weinheim/Bergstrasse 1982.