Quantum Chemical Calculations on Si_4H_4

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The ground state structure of Si_4H_4 is a cyclic bis(silanediyl) $(SiSiH_2)_2$; planar tetrasilacyclobuta-1,3-diene, however, does not correspond to a local minimum on the energy hypersurface.

A well known isomer of C_4H_4 is cyclobutadiene with a ^1A_g ground state and a planar, rectangular structure with alternating C–C bonds. It is well established that singlet cyclobutadiene cannot be regarded as an effectively square molecule, since the D_{4h} conformation is a saddle point lying 50 kJ/mol higher. The lowest excited state of cyclobutadiene is the $^3A_{2g}$ state (D_{4h} symmetry) which lies about 42 kJ/mol above the square singlet.[1] A further well known C_4H_4 isomer is the highly strained tetrahedrane which is 97 kJ/mol higher in energy than cyclobutadiene.[2] Hitherto, only substituted cyclobutadienes and tetrahedranes were known to be kinetically stable.[3]

When changing from C_4H_4 to its silicon analogue, Si_4H_4, one may expect a totally different situation since silicon is well known for its reluctance to form multiple bonds and its preference to adopt divalent structures instead. Therefore, we have concentrated our search on three types of Si_4H_4 isomers (Figure 1) which can be classified as (i) divalent (**1**), (ii) multiply bonded (**2**), and (iii) saturated (**3**). This is analogous to the treatment of the Si_6H_6 system.[4] The geometry optimization for configuration (**2**) was performed in D_{2h} (planar) and C_{2h} (nonplanar) symmetries. For the present calculations we used a modified version of the HONDO program system[5] for all geometry optimizations and the program system MOLEKEL[6] for configuration interaction calculations in conjunction with a local pseudopotential for the description of the silicon atom.[7] Except for the saturated structure and the high spin states, which were calculated at the monodeterminantal level, we used two-configurational (TC-SCF) reference wavefunctions throughout. All geometry optimizations were performed at the SCF and/or TC-SCF level with a triply split valence shell (s,p) basis for silicon and a corresponding (s) basis for hydrogen (basis A[7]). The effects of electron correlation have been taken into account by the method of configuration interaction (CI) where all single and double substitutions relative to the SCF (TC-SCF) reference wave functions have been included (CISD). The effects of unlinked quadruple substitutions (CISDQ) are estimated by the use of Davidson's formula.[8] For these calculations the basis was augmented by a set of d functions for silicon with an exponent of 0.35.

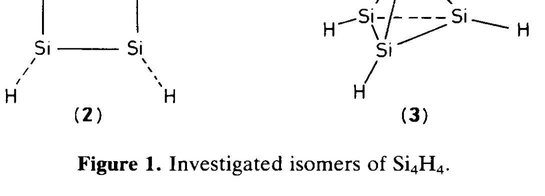
(**1**) (**2**) (**3**)

Figure 1. Investigated isomers of Si_4H_4.

The singlet state (**1**) (C_{2v} symmetry) was found to be the lowest energy isomer of Si_4H_4. A triplet state (C_{2v}) and a quintet state (D_{2h}) of (**1**) lie 69 and 242 kJ/mol, respectively, above the singlet (Table 1). At the SCF level the respective energy differences are 62 and 122 kJ/mol.

The planar conformer of (**2**) (tetrasilacyclobutadiene) is not a minimum on the singlet potential energy surface. Symmetry reduction from D_{2h} to C_{2h} by *trans* bending of the hydrogens leads immediately to a decrease in energy. At the optimized geometry the C_{2h} conformer is found 20 kJ/mol below the

Table 1. Relative energies of investigated conformers of Si_4H_4.

			Relative energy/kJ mol^{-1}		
Molecule	Multiplicity	Symmetry	SCF	CISD	CISDQ
(1)	1	C_{2v}	0.0	0.0	0.0
(1)	3	C_{2v}	62.3	69.8	69.4
(1)	5	D_{2h}	120.9	209.9	241.7
(2)	1	C_{2h}	153.5	132.6	121.3
(2)	1	D_{2h}	166.0	150.1	142.2
(3)	1	T_d	205.8	190.3	189.0

Table 2. Ring strain energies for cyclosilanes.

	Ring strain energy/kJ mol^{-1}	
Molecule	This work	Ref. 12
c-$(SiH_2)_3$	55	56
c-$(SiH_2)_4$	19	19
$(SiH)_6$	46	54[a]
$(SiH)_4$	93	101

[a] P. v. R. Schleyer, personal communication.

planar (D_{2h}) conformer and 121 kJ/mol above the ground state structure (**1**). No stable triplet state was found, however, which could be ascribed a C_{2h} structure resembling (**2**).

In the singlet state tetrasilatetrahedrane (**3**) corresponds to a minimum on the potential energy surface lying 189 kJ/mol above (**1**) and 24 kJ/mol above the planar conformer of (**2**). Using a basis set of double zeta quality with inclusion of d functions for silicon and p functions for hydrogen, Schaefer found 28 kJ/mol for the latter energy difference.[9] Geometrically, (**3**) obviously belongs to the class of strained molecules which are frequently characterized by the strain energy per bond. Using the homodesmotic reaction (1)[10] we calculated a

$$\text{4 tetrasilaisobutane} = \text{tetrasilatetrahedrane} + \text{6 disilane} \quad (1)$$

reaction energy of 562 kJ/mol from which a ring strain energy of 93 kJ/mol per bond can be derived. For comparison we give the strain energies per bond for three other molecules which can be regarded as strained cyclosilanes, namely cyclotrisilane, cyclotetrasilane, and hexasilaprismane (Table 2).

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