J. Phys. Chem. A **1999,** *103,* 5581−5584

Structure and Conformations of Cyclopentasilane, Si_5H_{10}

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Received: March 15, 1999

Three different conformations of cyclopentasilane, Si_5H_{10}, have been analyzed in detail using ab initio and density functional methods at the HF/B2, MP2/B2, CCSD/6-31G*, and B3LYP/B2 levels of theory. While the envelope (C_s) and the twist (C_2) forms have essentially the same energy, the planar form (D_{5h}) is ca. 1.3−2.9 kcal mol^{-1} less stable. The averaged computed Si−Si bond length of 2.356 Å (for C_s and C_2, each) is ca. 0.02 Å larger than the r_e value of 2.332 Å derived from an electron diffraction study.

Introduction

Cyclopentane has been extensively studied by a variety of techniques since 1947 when Kilpatrick, Pitzer, and Spitzer[1] introduced the concept of pseudorotation (see also the 1993 paper by Allinger et al.[2] and references therein). However, its silicon analogue, cyclopentasilane (CPS), Si_5H_{10}, has received much less attention, in part because CPS was only synthesized in 1975[3] (see also the 1995 review paper by Hengge and Janoschek[4]).

In 1976, the structure of Si_5H_{10} was established by gas-phase electron diffraction[5] and the vibrational spectra were reported.[6] In 1987, Grev and Schaefer were the first to calculate by ab initio quantum mechanical methods the structure of Si_5H_{10} together with Si_3H_6 and Si_4H_8.[7] This series of cyclosilanes studied theoretically was extended to cyclohexasilane, Si_6H_{12}, in 1994.[8] The authors of the latter paper tried to compare the C−C and Si−Si distances in analogous cyclic systems following an idea outlined earlier by Mastryukov.[9] They found an overall agreement between theory and experiment except for cyclotrisilane and cyclopentasilane.

In 1994, Tossell, Winkler, and Moore[10] concluded that the ab initio geometries for $Si_4(CH_3)_8$, Si_5H_{10}, and Si_6H_{12} “are in good, but not perfect, agreement with experiment”. In 1995, a paper by Leszczynski et al.[11] addressed the same issue: Is there a discrepancy between experiment and theory? These authors found that for Si_2H_6, H_3SiGeH_3, and Ge_2H_6 correlated levels of theory (CCSD, CISD, MP2) used in conjunction with valence triple-ζ basis sets augmented by f-polarization functions on heavy atoms are capable of reproducing all experimental structural parameters that are well established.

In all the previous studies mentioned above,[7,8,10,11] theoretical results were directly compared with experimental structures. However, quantum mechanical calculations give the equilibrium structure (r_e) while electron diffraction (ED) yields some kind of thermally averaged parameters (r_a or r_g).[12,13] There were several attempts in the past to relate theory to experiment using either a rigorous approach[14,15] or a purely empirical treatment.[16] Recently, Ma et al.[17] suggested still another way; they used MM3 and MM4 force fields to convert r_g to r_e values. These authors made some general comments which are relevant to the present study.

(1) The bond lengths generally shrink with increasing basis set quality but lengthen with an increasing level of correlation [from MP2 to CCSD and CCSD(T)]. The inclusion of f functions has significant effects on the bond lengths, but the hydrogen d functions have no noticeable effects. The CCSD(T) bond lengths are generally 0.003−0.006 Å longer than those at the CCSD level.

(2) The B3LYP/6-31G* method gives bond lengths involving second-row atoms that are significantly too long. Very large basis sets are required to give accurate values for such bond lengths. For example, even at the B3LYP/6-31G(3df,2p) level, the C−S bond length for dimethyl sulfide is still 0.007 Å longer than the experimental r_g value. Therefore, the MP2/6-31G* method is recommended for calculating bond lengths involving second-row atoms.

The present investigation is motivated by the continuing interest of our research group in computing molecular structures containing second-row elements using high levels of theory. We thus decided to apply DFT (B3LYP/B2) and ab initio (MP2/B2 and CCSD/6-31G*) methods to accurately study the conformations of cyclopentasilane.

Computational Method

The structures were geometry optimized within the given symmetry point group with the Gaussian 94 program[18] at the HF, MP2, and CCSD levels of theory.[19] A basis set “B2”, which is (12s9p2d/6s5p2d) for Si and (6s2p/4s2p) for H, as described in ref 20, was used at HF and MP2. The “frozen core approximation” was applied for MP2 computations. Pople’s 6-31G* standard basis set was applied for the coupled cluster calculations including single and double excitations (CCSD). For DFT (density functional theory) calculations, Becke’s three-parameter exchange functional[21] together with the correlation functional by Lee, Yang, and Parr[22] (B3LYP) was used as implemented in Gaussian 94 together with the B2 basis set. Vibrational frequencies were evaluated analytically at the HF/B2 and B3LYP/B2 levels.

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10.1021/jp990901y CCC: $18.00

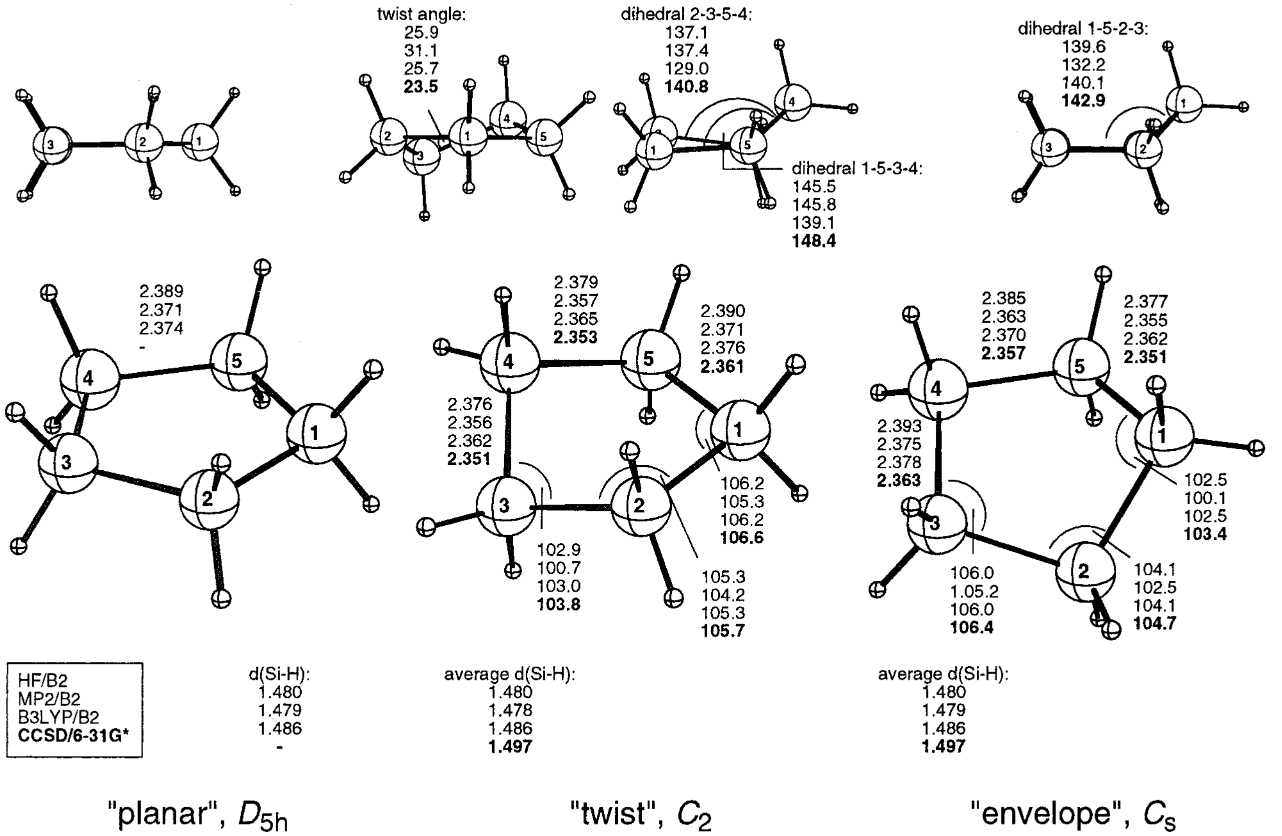


Figure 1. Structures of cyclopentasilane, Si_5H_{10}, with geometries optimized at different levels of theory: planar (D_{5h}), twist (C_2), and envelope forms (C_s). All distances are in angstroms, all angles are in degrees. The preferred level of theory, CCSD/6-31G*, is given in boldface type. The planar structure was not optimized at the CCSD level since it is a stationary point of Hessian index 2.

TABLE 1: Averaged Si−Si Bond Lengths[a] [Å] and Relative Energies [kcal mol^{-1}] of the Planar (D_{5h}), Twist (C_2), and Envelope (C_s) Conformations of Cyclopentasilane, Si_5H_{10}, Computed at Different Levels of Theory

	D_{5h}	C_2	C_s
	HF/B2		
Si−Si	2.389	2.383	2.383
E_{rel}[b]	1.50	0.0	0.0
	B3LYP/B2		
Si−Si	2.374	2.369	2.368
E_{rel}[c]	1.30	0.0	0.01
	MP2/B2		
Si−Si	2.371	2.362	2.362
E_{rel}[d]	2.87	0.0	0.01
	CCSD/6-31G*		
Si−Si		2.356	2.356
E_{rel}[d]		0.0	0.0

[a] Experiment: r_a(Si−Si) = 2.342(3) Å;[5] r_e(Si−Si) = 2.332 Å (see text). [b] Relative energy, corrected by scaled (0.89) zero-point vibrational energy. [c] Relative energy, corrected by zero-point vibrational energy. [d] Relative energy without correction for zero-point vibrational energy.

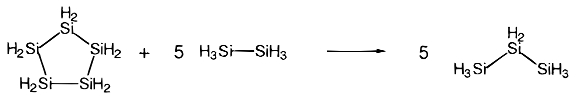
Results and Discussion

Three conformations of CPS were considered, namely planar (D_{5h}), twist (C_2), and envelope (C_s). Some important geometrical parameters are displayed in Figure 1. The average Si−Si bond lengths and relative energies for each conformation are listed in Table 1.

The D_{5h} form was characterized as a second-order stationary point with the HF (68i cm^{-1}, E_2'') and B3LYP (62i cm^{-1}, E_2') methods and is 2.9 kcal mol^{-1} higher in energy (at the MP2/B2 level) than the twist and envelope conformers, which have essentially the same energy at all levels employed (including CCSD/6-31G*). The Cartesian coordinates of these two conformers are deposited as Supporting Information. Two opposing contributions to this energy difference can be identified.

a. Relief of Pitzer Strain. By moving Si1 out of the Si2−Si3−Si4−Si5 plane the envelope form avoids four of the five eclipsed arrangements of SiH_2 groups; two groups centered at Si3 and Si4 are still eclipsed (see projection in Figure 1). Distortion to the twist form avoids all eclipsed arrangements, although it still leaves some relatively small H−Si−Si−H dihedral angles, e.g., 14.8° and 15.1° for H−Si1−Si2−H at CCSD/6-31G*. All this is accompanied by shortening of the (average) Si−Si bond lengths by 0.009 Å (at MP2/B2).

b. Increase of Bayer Angular Strain. In the planar form, the Si−Si−Si bond angle is 108°, while other conformers systematically display bond angles 1.5−5.5° smaller than this. In open-chain silanes as well as in hydrocarbons, the Si−Si−Si and C−C−C angles, respectively, are larger than the tetrahedral value; for example, the Si−Si−Si bond angle in Si_3H_8 is 111.9° at MP2(fu)/6-31+G*). The total remaining ring strain for cyclopentasilane, Si_5H_{10} (C_s and C_2 conformers are equal in energy), may be estimated to be 4.4 kcal mol^{-1} (CCSD/6-31G*) by the following homodesmotic eq 1.



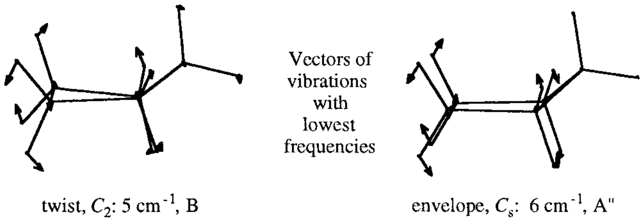
(1)

Careful examination of molecular models of the twist and envelope conformers reveals their hidden similarity. To illustrate this, two different projections are presented for the twist form at the top of Figure 1. One is the usual representation along the

C_2 symmetry axis, while the other projection shows that the twist conformer actually also looks like a distorted envelope. Looking at the molecule in this way, one realizes that only a slight distortion is needed for a conformational transformation

$$\text{twist } (C_2) \rightleftharpoons \text{envelope } (C_s) \qquad (2)$$

The four silicon atoms that are in one plane in the envelope (Si2−Si3−Si4−Si5) deviate from planarity by approximately 8° (compare dihedral angles given in Figure 1). The lowest vibrational frequencies computed at HF/B2 are very small for both the twist (C_2, 5 cm^{-1} B) and the envelope (C_s, 6 cm^{-1} A″) conformer.



These vibrations correspond to the motion for the conformational change shown in eq 2. (B3LYP even gives small imaginary vibrational frequencies for both conformers, but this is likely to be an artifact of the numerical integration.) Although we did not locate the transition structure for the twist to envelope rearrangement, we conclude that this is an extremely facile process. The relative energy of the planar form, a second-order stationary point (2.9 kcal mol^{-1} at MP2/B2; 1.3 kcal mol^{-1} at B3LYP/B2), is an upper bound for the barrier.

Although the conformational change has some effect on individual Si−Si distances, the average values are essentially identical for C_2 and C_s resulting in 2.356 Å at our highest level of theory (CCSD/6-31G*). Leszczynski et al. computed 2.328 and 2.331 Å for the Si−Si distance in Si_2H_6 at CCSD/DZP and CCSD/TZP(f,d), respectively.[11] A similair increase of ca. 0.003 Å in the (averaged) Si−Si distance can be expected for cyclopentasilane with a much larger basis set at CCSD. However, such a level of theory is not achievable for cyclopentasilane at present. Nevertheless, the best theoretical result of 2.356 Å is relatively close to the $r_a = 2.342(3)$ Å from an electron diffraction analysis.[5] On the other hand, as was mentioned in the Introduction, it is conceptually better to compare r_e and r_g parameters reduced to the same basis. Different procedures[12−17] can be used for this purpose. However, we follow another approach here.

For a Morse oscillator in its ground state, it may be shown[23,24] that the ED parameter r_a and the equilibrium bond length r_e are related by

$$r_e \approx r_g - (3/2)au^2 = r_a + (u^2/r) - (3/2)au^2 \qquad (3)$$

where a is the Morse asymmetry constant and u is the amplitude of vibration. The terms u^2/r and $(3/2)au^2$ represent harmonic and anharmonic corrections, respectively. The asymmetry parameter a is usually fixed at 2 Å^{-1} for bonds not involving hydrogen and at 3 Å^{-1} for bonds involving hydrogen.[25] Utilizing parameters reported in the ED study of CPS[5] (r_a(Si−Si) = 2.342 Å and u(Si−Si) = 0.062 Å) and using eq 3 we may estimate r_e from experiment to be 2.332 Å. When this corrected experimental value is used, the difference between theory and experiment increases to 0.024 Å. This observation is in agreement with other comparisons of measured and calculated Si−Si bond lengths. Table 2 lists some examples from which it is clear that theory normally "overshoots" experiment. The only exception is the result with the STO-3G basis set for $Si_3Br_6H_2$. However, this basis set is too small to give meaningful results.

TABLE 2: Comparison of Si−Si Bond Lengths: Experiment and Theory

molecule	experiment	ref	theory	ref
Si_2H_6	2.331(3)	26	2.368, HF (2d,2p) 2.331, CCSD TZP(f,d)	11
$Si_2Cl_4H_2$	2.307(8)	27	2.337, MP2/6-31G* 2.339, MP4(sdq)/6-31++G(d,p)	27
Si_3H_8	2.332(2)	28	2.337, MP2/6-31G*	28
$Si_3Br_6H_2$	2.331(18)	29	2.373, HF/SBK-ECP 2.277, STO-3G	29
Si_4H_{10}	2.337(3)	28	2.359, 6-31G*	28

Conclusion

Two minimum conformers of cyclopentasilane, Si_5H_{10} (twist, C_2, and envelope, C_s) have essentially the same energy. The planar D_{5h} symmetric form is a second-order stationary point, 2.9 kcal mol^{-1} higher in energy (MP2(fc)/B2; 1.3 kcal mol^{-1} at B3LYP/B2). Hence, CPS undergoes pseudorotation like its carbon analogue, cyclopentane.[1,2] The averaged Si−Si bond lengths show no significant differences between C_s and C_2 for our levels of theory employed, and we notice a decrease in the order HF/B2 > B3LYP/B2 > MP2(fc)/B2. The best agreement with our estimate of $r_e = 2.332$ Å from electron diffraction is found for CCSD/6-31G* (2.356 Å).

Acknowledgment. One of the authors (V.S.M.) thanks Professor J. E. Boggs and Professor M. Fink for helpful discussions. Financial support from The Robert A. Welch Foundation is gratefully acknowledged. H.F.S. was supported by the U. S. National Science Foundation. We thank K. Hagen and T. H. Johansen for helpful correspondence. M.H. is grateful to the Deutscher Akademischer Austauschdienst for a postdoctoral fellowship.

Supporting Information Available: Cartesian coordinates of twist and envelope Si_5H_{10} conformers, optimized at the CCSD/6-31G* level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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