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Tetrasilatetrahedrane

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Abstract: Ab initio self-consistent-field theory has been applied to tetrasilatetrahedrane, the T_d symmetry isomer of Si_4H_4. The use of double-ζ (DZ) and double-ζ-plus polarization (DZP) basis sets allows prediction of the structure of tetrasilatetrahedrane: r_e(Si–Si) = 2.395 Å, r_e(Si–H) = 1.472 Å (DZ SCF); r_e(Si–Si) = 2.308 Å, r_e(Si–H) = 1.464 Å (DZP SCF). Harmonic vibrational frequencies are also predicted and show that tetrasilatetrahedrane is a minimum-energy isomer of Si_4H_4 and, thus, may be experimentally observed.

We have recently reported[1] an ab initio theoretical study on hexasilabenzene (Si_6H_6), the silicon analogue of benzene, and concluded that, despite the existence of a local D_{6h} minimum energy structure, hexasilabenzene contains little aromatic stabilization, on the basis of simple bond strength (ΔE_{SCF}) arguments. In addition, the presence of a very low frequency (10 cm^{-1}) normal-mode vibration indicates for hexasilabenzene the preference shown by other silicon-containing compounds for pyramidalization at tricoordinate silicon.[2,3] Other recent results by Nagase, Kudo, and Aoki[4] have confirmed that there are lower lying Si_6H_6 isomers which contain fewer trivalent (i.e., multiple-bonded) silicon atoms. On the basis of these recent results,[1,4] as well as earlier studies of other unsaturated silicon-containing molecules,[3] it is not unreasonable to postulate that, of Si_4H_4 isomers, tetrasilatetrahedrane (Tricyclo[1.1.0.0^{2,4}]tetrasilane) might be the most energetically preferred.

This assumption, of course, contrasts the behavior of unsaturated silicon and carbon compounds. In a thorough examination of the C_4H_4 surface using the MNDO method, Kollmar, Carrion, Dewar and Bingham[5] found many isomers lower in energy than tetrahedrane, including the anti-aromatic cyclobutadiene. This reemphasizes the preference of carbon compounds for multiple (double or triple) bonds rather than small (strained) rings, even at the expense of anti-aromatic (or other electronic) destabilization. The relative stability, however, of cyclopolysilanes and cage silicon structures[6] rather than disilenes[3a–d] or the unknown disilynes[3e,f] might lead one to prefer tetrasilatetrahedrane (or its derivatives) as a likely stable species on the Si_4H_4 potential energy surface and to point research efforts, both theoretical and experimental, toward this interesting and potentially unusual molecule. The recent report by Masamune et al.[7] of the synthesis of bicyclo[1.1.0]tetrasilane derivatives certainly indicates synthetic activity toward and interest in tetrasilatetrahedrane.

We have undertaken, then, and report here an ab initio self-consistent field (SCF) investigation of tetrasilatetrahedrane, the T_d symmetry isomer of Si_4H_4. We have employed the standard contracted Gaussian basis sets of Huzinaga[8] and Dunning and Hay.[9] Hydrogen atom functions were scaled by a factor of 1.2 before contraction. This double-ζ (DZ) quality basis may be labeled Si(11s7p/6s4p), H(4s/2s) by using common notation. A set of polarization functions [α_d(Si) = 0.50, α_p(H) = 0.75] was added to form a double-ζ-plus polarization (DZP) basis, denoted Si(11s7p1d/6s4p1d), H(4s1p/2s1p). The DZ basis consists of 80 and the DZP of 116 contracted functions. We have completely optimized the geometry of tetrasilatetrahedrane using SCF analytic energy first-derivative methods,[10] with residual forces being less than 10^{-7} hartree/bohr. The stationary points were characterized by evaluation of the SCF Hessian (force constant) matrix by analytic second-derivative techniques.[11] All of the results reported here were determined at geometries constrained to T_d symmetry; however, all theoretical endeavors were actually performed in the D_2 subgroup of T_d. The valence electronic configuration of tetrasilatetrahedrane is

$$...(4a_1)^2(6t_2)^6(5a_1)^2(7t_2)^6(2e)^4 \tag{1}$$

in T_d symmetry, or, in D_2 symmetry

$$...(6a_1)^2(6b_1)^2(6b_2)^2(6b_3)^2(7a_1)^2(7b_1)^2(7b_2)^2(7b_3)^2(8a_1)^2(9a_1)^2 \tag{2}$$

Table I. Energies, geometrical Parameters, Harmonic Vibrational Frequencies, and Intensities (in Parentheses) for Tetrasilatetrahedrane (Si_4H_4)[a]

	DZ	DZP
E_{SCF}	−1157.694386	−1157.828397
r_e(Si–Si)	2.395	2.308
r_e(Si–H)	1.472	1.464
ν_1 (A_1, Si–H sym str)	2362	2399
ν_2 (A_1, Si–Si sym str)	546	612
ν_3 (E, asym cage torsion)	562	467
ν_4 (E, sym cage torsion)	335	306
ν_5 (T_2, Si–H asym str)	2353 (91.8)	2391 (77.2)
ν_6 (T_2, cage rocking)	591 (70.1)	579 (72.7)
ν_7 (T_2, Si–Si asym str)	442 (5.83)	461 (0.008)
ν_8 (T_2, Si–H bend)	399 (0.00)	433 (0.000)

[a] Energies are given in hartrees, bond lengths in Å, frequencies in cm^{-1}, and intensities in km/mol. The predicted harmonic vibrational frequencies are expected to be about 10% higher than the true fundamentals.[21]

Our results for the structure of tetrasilatetrahedrane are given in Figure 1 and in Table I. The Si–Si bond length of 2.395 Å (at the DZ level) is slightly long (~0.01 Å) compared to previously theoretically determined Si–Si single bond distances.[12] The addition of polarization functions, however, causes a significant bond shortening, by 0.087 Å, to give a Si–Si distance which is, in fact, among the shortest known Si–Si single bonds.[13–15] Al-

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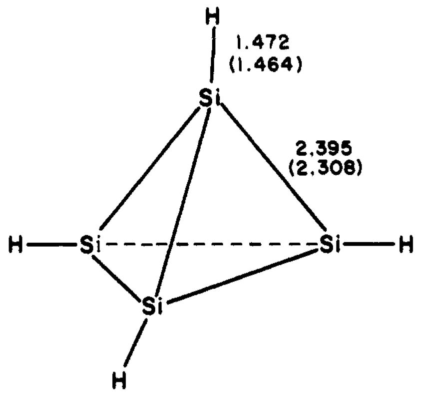

Figure 1. Structure of tetrasilatetrahedrane (Si_4H_4). Bond lengths at the DZ (DZP) self-consistent field level of theory are given in angstroms.

though some bond shortening is expected with the inclusion of polarization functions,[16] and although it is known that higher angular momentum (i.e., polarization) functions are necessary for the proper description of bonding between second row atoms (e.g., silicon), this shortening may possibly indicate strain in tetrasilatetrahedrane, with the strained (bent) bonds being only properly described by the use of a polarized basis.

In order to test whether this bond shortening was due to polarization functions or simply to having additional functions (i.e., saturation of the basis set), we have reoptimized the structure of tetrasilatetrahedrane with a full triple-ζ (TZ) basis set, Si-(12s9p/9s6p),[17] H(5s/3s).[18] The equilibrium geometry found, r_e(Si–Si) = 2.374 Å and r_e(Si–H) = 1.469 Å, indicates some bond shrinkage with the expanded sp basis but not as much as that caused by a set of polarization functions. This finding serves to confirm the suggestion that molecules containing second-row atoms, particularly molecules that may have some ring strain, do, in fact, require polarization functions to properly describe their bonding. In other silacyclic rings which may contain a reasonable degree of strain, for example, silacyclobutadiene (SiC_3H_4)[19] and cyclotrisilane (Si_3H_6),[20] the bond shortening upon addition of polarization functions to the basis set is 0.096 (Si–C) and 0.056 (Si–Si) Å, respectively.

The predicted harmonic vibrational frequencies for tetrasilatetrahedrane are also presented in Table I. All of the eigenvalues of the SCF Hessian matrix are positive (with both basis sets) indicating that the predicted symmetrical structure for tetrasilatetrahedrane is a minimum-energy structure on the Si_4H_4 potential energy surface. The estimated fundamental frequencies, ~10% lower than the ab initio harmonic frequencies,[21] and the corresponding infrared intensities[22] should also be useful for the spectroscopic characterization of tetrasilatetrahedrane. In particular, the estimated 521-cm^{-1} t_2 symmetry cage rocking mode (ν_6) is substantially higher in energy than a typical Si-Si stretching mode (434 cm^{-1} in Si_2H_6, for example)[23] and is relatively intense. The remaining (IR) active (t_2 symmetry) modes seem less characteristic, of lower frequency, and likely to overlap experimentally with other Si-Si bands.

Thus, we have predicted a symmetric (T_d) minimum energy structure for tetrasilatetrahedrane. Because of the bonding preference indicated previously by unsaturated silicon compounds (pyramidal, singly bonded)[1,3,4] this structure may be reasonably predicted a priori as one of the lower lying Si_4H_4 isomers. In addition, we can now confidently predict that the tetrasilatetrahedrane cage structure is a stable one, a local minimum, and, thus, may be synthesized and/or spectroscopically characterized. Because of the current direction of synthetic silicon chemistry,[7] we feel a successful synthetic approach to the tetrasilatetrahedrane skeleton may be imminent, and we await experimental interrogation of our predictions.

In investigations of other portions of the Si_4H_4 potential energy surface, we have also located a D_{2h} symmetry (cyclobutadiene-like) stationary point. Although we intend to publish a thorough discussion of the character of the entire Si_4H_4 potential energy surface,[24] we feel a few comments may be useful here. In particular, the D_{2h} stationary point lies 11.0 (3.1) kcal/mol lower in energy than tetrasilatetrahedrane and, in addition, has imaginary vibrational frequencies of 173(151)i and 214(157)i cm^{-1} at the DZ SCF (DZP SCF) level of theory. The two imaginary normal modes are out-of-plane motions, a result that is not surprising in light of the previously noted preference of disilenes (and disilynes) for unusual, nonplanar geometries.[1,3] We suspect that lower symmetry, nonplanar structures may, in fact, be quite important in the overall description of the Si_4H_4 potential energy surface.[24]

Although the effects of correlation have been estimated to be relatively small for the comparison of cyclobutadiene and tetrahedrane[27] and of silacyclobutadiene and silatetrahedrane,[25] we have considered the effect of correlation on the relative energies of tetrasilatetrahedrane and tetrasilacyclobutadiene at the DZ SCF and DZP SCF stationary points, particularly in light of the fact that a two-configuration (TC) SCF or small CI treatment has been found useful in the study of silacyclobutadiene.[19,26] Specifically, we have included correlation effects through the use of configuration interaction including all single and double excitations (CISD). However, the 20 lowest lying MO's (Si 1s-, 2s-, and 2p-like orbitals) are required to be doubly occupied at all times, and the corresponding virtual orbitals are left unoccupied; thus, the DZ (DZP) CI includes 11 479 (54 949) (D_2) and 6571 (29 701) (D_{2h}) interacting walks. At the CISD level of theory tetrasilacyclobutadiene lies 15.4 (4.5) kcal/mol lower in energy than tetrasilatetrahedrane, that is, it is more stable by 4.4 (1.4) kcal/mol than at the DZ (DZP) SCF level. By the use of Davidson's formula for unlinked quadrupole excitations,[28] tetrasilacyclobutadiene lies at −17.9 (−6.3) kcal/mol relative to tetrasilatetrahedrane.[29] Thus, although the relative energies may change somewhat with optimization at the CISD level, it is seen that correlation does not dramatically favor either isomer in this case.[25,27]

Last, since tetrasilatetrahedrane is not the global minimum energy isomer of Si_4H_4 (although it is a local minimum energy structure), one must comment on the interconversion of tetrasilatetrahedrane and the remainder of the potential energy surface. First, dissociation to two molecules of disilyne[1,3] is forbidden by symmetry and, thus, is certainly associated with a large barrier (as has been suggested previously for tetrahedrane[27] and silatetrahedrane[25]). Second, conversion of tetrasilatetrahedrane to tetrasilacyclobutadiene (which may be considered the first step of a two-step dissociation to disilyne) is also a symmetry-forbidden (4π-electron) process and is, therefore, almost certainly associated

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(29) By use of the DZ basis,[8,9] E_{SCF} (Si_4H_4 (D_{2h})) = −1157.711 919, E_{CI} = −1157.944 589, E_{DVD} = −1157.981 402; the optimized structure is r_e(Si—Si) = 2.448 Å, r_e(Si═Si) = 2.155 Å, r_e(Si—H) = 1.471 Å, θ_e(HSi—Si) = 132.7°. For tetrasilatetrahedrane, E_{CI} = −1157.919 987, E_{DVD} = −1157.952 826. With the DZP basis, E_{SCF}(D_{2h}) = −1157.833 300, E_{CI} = −1158.176 968, E_{DVD} = −1158.232 680, r_e(Si—Si) = 2.349 Å, r_e(Si═Si) = 2.118 Å, r_e(Si—H) = 1.465 Å, θ_e(HSi—Si) = 131.8°; for tetrasilatetrahedrane, E_{CI} = −1158.169 865, E_{DVD} = −1158.222 597.

as well with a large barrier (as is, in fact, the second step, tetrasilacyclobutadiene → disilyne). Thus, the fact that other Si_4H_4 minima, both singlets and high-spin states,[24] exist does not preclude the possibility of an experimentally observable T_d symmetry species Si_4H_4 (or its derivatives) which is at least somewhat kinetically stable (i.e., connected by a large barrier to other isomers). In fact, the possible existence of other stable Si_4H_4 isomers should stimulate additional experimental research directed toward the observation of other lower symmetry isomers of Si_4H_4 (or its derivatives).

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Quantum Mechanical Stability of Reaction Coordinate in the Unimolecular Reaction of Silanone

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Abstract: A dynamical aspect of the unimolecular dissociation reaction of silanone is analyzed. A global feature of the potential energy surface as a function of the internal coordinates of the nuclear configurations is revealed. The reaction has the negative force constant of out-of-plane vibrational mode orthogonal to the reaction coordinate. Then a new notion of the quantum mechanical stability is discussed. The dynamic features of the reaction are characterized by tunneling crossover and multistep isotope effect.

I. Introduction

Recently, theoretical studies of chemical reaction dynamics have received much attention.[1] The reason why the theoretical treatment of chemical reaction dynamics is so attractive is the existence of various rearrangement channels even for a system of a fixed number of nuclei on a single potential energy surface. In this connection, differential geometrical studies[2] and topological studies[3] of chemical reaction systems have recently been developed. The global feature of the potential energy surface as a function of the internal coordinates of the nuclear configuration is central to this direction of research, because the dynamism of the reactive flux of a chemical reaction reflects the characteristic features of the potential energy surface. The fundamental role of the IRC (intrinsic reaction coordinate)[4] as the central line of the reactive flux in the internal coordinate space has been widely demonstrated; the IRC is defined by the differential equation for a unique curvilinear reaction coordinate which connects reactant and product via a transition state on the potential energy surface. Reaction dynamics along the IRC (or meta-IRC[2] for excited-state chemical reactions) is studied by the combination of the promoting mode in the direction of the IRC and the vibrational modes in the direction orthogonal to the IRC.[1b,2,5]

In our previous work,[5] we have investigated the "stability" of the IRC in the unimolecular decomposition reaction of H_2CS and found the *negative* force constant of the out-of-plane vibrational mode orthogonal to the IRC in the early stage of the reaction. This shows that the motion of the representative particle on the IRC becomes unstable in the direction of the out-of-plane vibrational mode. This will broaden the area accessible for reactive flux to pass through the transition state. The problem of reaction coordinate instability has recently been observed in the literature from various viewpoints: in terms of the topology of potential energy surfaces,[3a] in terms of the statistical mechanics and symmetry properties of reaction systems,[4b–d] and in terms of the intrinsic field theory of environment effects.[2c]

In the present paper, we shall study the *quantum mechanical* treatment of the vibrational motions orthogonal to the IRC. Remarkably, the zero-point energy may be *negative* on the IRC. This is called the *quantum mechanical instability* of the reaction coordinate. The dynamical aspect of the new notion of the quantum mechanical stability is discussed. The relationship with the "classical" stability criterion as studied in our previous work[5] is also shown. In order to clarify the present treatment, we shall examine the unimolecular decomposition reaction of silanone,

$$H_2SiO \rightarrow H_2 + SiO \qquad (I.1)$$

and its isotope effects, as compared with the well-known corresponding reaction of H_2CO and H_2CS.[5,6] Silanone itself has recently been identified by experiment,[7] but the reaction dynamics

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