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A THEORETICAL STUDY OF THE EFFECT OF SILICON SUBSTITUTION ON HYDROCARBON ACIDITY

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Summary

Ab initio molecular orbital calculations with double-zeta basis sets show the relative stabilities of three tautomers on the C_2SiH_4 energy hypersurface to be 3-silapropyne > 1-silaallene > 1-silapropyne. Comparison with literature values shows 1-silaallene to be more stable than 2-silaallene. Assuming deprotonation at carbon then the order of acidity is 1-silapropyne > 1-silaallene > 3-silapropyne > silaethane > silaethylene. For silaethylene and silaethane deprotonation occurs more easily at silicon than at carbon, while for both silapropynes and 1-silaallene carbon deprotonation is slightly favoured. The α-silyl group enhances the acidity of the adjacent methyl group and a silyl group in conjugation with a carbon—carbon triple bond enhances the acidity of the alkynyl proton. The methyl, ethyl, and 2-silaethyl groups all weakly decrease the acidity of the alkynyl proton.

Introduction

Recently, there has been considerable experimental and theoretical interest in hydrocarbons in which one of the carbon atoms is replaced by a silicon. Silicon has less of a tendency to be tetravalent than carbon and also tends to avoid multiple bonds, with the result that structures expected on the basis of carbon chemistry are not always the most stable. For instance on the $CSiH_2$ energy hypersurface vinylidenesilylene is the most stable [1,2], on the $CSiH_2$ hypersurface the structure containing a monovalent silicon is most stable [2], on the $CSiH_4$ hypersurface methylsilylene is of comparable stability to silaethylene [3], and on the $CSiH_5^+$ hypersurface only one tautomer, the methylsilyl cation is at a minimum [4].

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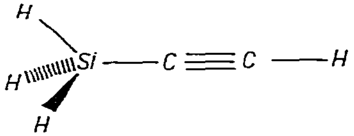
Recent theoretical work [5] on some isomers of C_2SiH_4 has shown 3-silapropyne (I) to be the most stable species on this energy hypersurface. The synthesis of this molecule was first reported in 1963 [6] and the compound has been well characterised [7]. Trimethylsilylethyne (I in which the hydrogens on silicon are replaced by methyl groups) is considerably more acidic than propyne [8], and α-trimethylsilylmethyl carbanions are sufficiently stable to be useful intermediates in synthesis [9—11]. Silicon is more electropositive than carbon and the trimethylsilyl group might therefore be expected to be less electron-withdrawing than the t-butyl group. This is not the case and the electron-withdrawing ability of the trimethylsilyl group is often explained either in terms of ($p \rightarrow d$) π-donation from the carbanion centre into the low-lying empty *d*-orbitals on silicon [9—11], or hyperconjugation between the silicon—carbon bonds and the lone pair at the carbanion centre [12].



(I)

Few silicon-containing hydrocarbons have, as yet, been synthesised, perhaps because chemical intuition based on a knowledge of carbon chemistry is not effective at predicting the relative stabilities of such molecules. Ab initio molecular orbital theory has been very successful in reproducing structures and heats of reactions for molecules containing atoms from the first full row of the periodic table, and should be equally reliable when applied to molecules containing second row elements. It should now, therefore, be possible to use ab initio molecular orbital theory to predict, from examinations of energy hypersurfaces not yet explored experimentally, which molecules should be sufficiently stable to synthesise. In order to assist the organosilicon chemist in identifying such molecules and also to study the effect on hydrocarbons of substituting a silicon for a carbon atom, we have undertaken a systematic study of molecules containing one silicon atom connected to carbon. As part of this study we now report the relative energies of some isomers on the C_2SiH_4 and $C_2SiH_3^-$ energy hypersurfaces and compare them with the analogous C_3H_4 and $C_3H_3^-$ surfaces. This has led to a study of the interaction between a silicon atom and an adjacent carbanion centre and, in this context, we have examined the effect of conjugation by computing the acidities of the conjugated 3-silapropyne and the unconjugated 4-sila-1-butyne systems. We have also examined the effect of silicon substitution on acidity by comparing the following pairs of acids: silaacetylene and acetylene; silaethylene and ethylene; silaethane and ethane; 3-silapropyne and propyne; and 1-silaallene and allene.

Methods

All calculations were for closed shell singlets. The primitive gaussian basis set used throughout the geometry optimisations consists of 11^s7^p functions on Si, 9^s5^p functions on C, and 4^s functions on H, all contracted to a double-zeta basis set [13,14]. This basis set was augmented by the following polarisa-

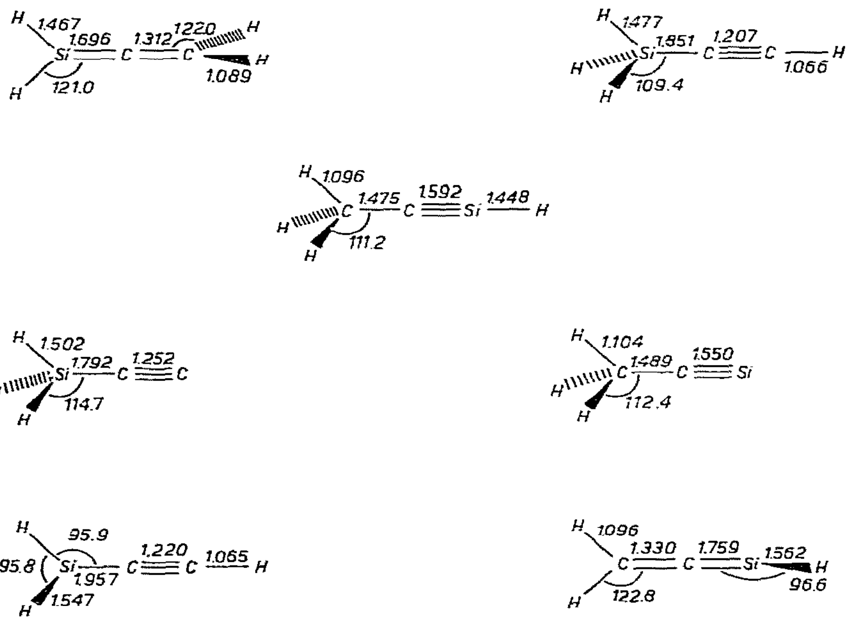


Fig. 1. Geometries as optimised with the double-zeta basis set for tautomers of C_2SiH_4 and of $C_2SiH_3^-$. Bond lengths are in Å and angles in degrees.

tion functions: a set of *d*-orbitals on C, exponent 0.7; a set of *d*-orbitals on Si, exponent 0.4; a set of *p*-orbitals on H, with exponent 0.433 when the hydrogen was attached to silicon, and 0.75 when the hydrogen was attached to carbon [15]. All the geometry optimisations used the gradient method [16,17] incorporated in the MONSTERGAUSS 80 program [18].

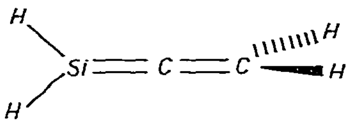
Results

a) Geometries

The structures of the isomers C_2SiH_4 and $C_2SiH_3^-$ are given in Fig. 1. Comparison with experimental geometries is possible only with 3-silapropyne (I), where there is good agreement. (Experimental values are C—Si 1.826 Å, C—C 1.208 Å, C—H 1.058 Å, Si—H 1.488 Å, and C—Si—H 108.7° [1].) The largest discrepancy between theory and experiment is in the carbon—silicon bond length where the experimental value is 1.826 Å, as opposed to the computed value of 1.851 Å. In this respect we note that in the only previous theoretical treatment of this molecule this bond was computed to be 1.856 Å [5].

In 1-silaallene (II) the methylene fragment has very similar geometry to allene [19], but in the silylene fragment the carbon—silicon bond is considerably longer than in silaethylene (1.696 Å as opposed to 1.587 Å [20]). In 1-silapropyne (III) the geometry around silicon is similar to that of silaacetylene [1] and at the methyl group is similar to propyne [21].

In the anions the bond lengths are generally slightly longer than in their parent acids, as is usual on deprotonation. Removal of the alkynyl proton of



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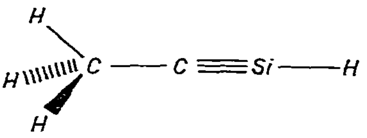
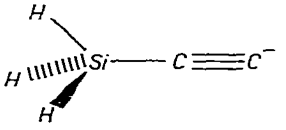


(III)

3-silapropyne, however, results in a decrease (by 0.059 Å) of the carbon—silicon bond and this is attributable to an increased interaction between the π-system of the triple bond and the silyl group in IV. Removal of a methylene proton from 1-silaallene produces large structural changes with the silylene fragment becoming pyramidal, the silicon—carbon bond increasing by 0.261 Å



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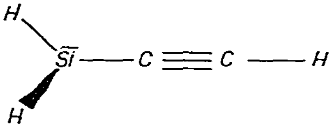
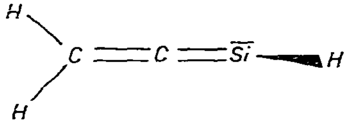


(V)

and the carbon—carbon decreasing by 0.092 Å. This anion is best described by the valence bond structure V. The angle between the bisector of H—Si—H and the bond to the substituent is 98.8°, giving an out-of-plane angle of 81.2°. This is slightly smaller than the angle in SiH_3^-, but a little larger than in the anions SiH_2X^-, where X = CH_3, NH_2, OH and F [22].

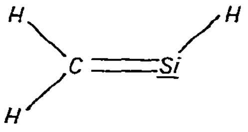
Deprotonation of the silylene group of 1-silaallene results in an anion, VI,



(VI)

which is structurally similar to 1-silaallene. In this respect deprotonation of the methyl group of 1-silapropyne results in similar structural changes as occur in the deprotonation of allene [23]. In VI the carbon—carbon bond length is similar to that in ethylene [24] while the carbon—silicon distance is slightly larger than the bond is silaethylene [20], suggesting that the ion is best described in terms of two double bonds rather than a single and triple bond.

The structures of the two possible anions, VII and VIII, formed by deprotonation of silaethylene, both assumed to be planar in the optimisation, are given in Fig. 2. Both have slightly longer bond lengths than silaethylene (C—Si 1.715 Å, C—H 1.075 Å, and Si—H 1.474 Å [20]). Removal of a proton from the silylene group results in a much smaller ∠ C—Si—H for the remaining hydrogen



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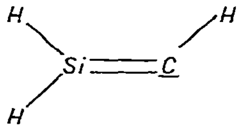

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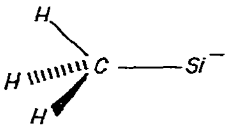

(IX)

and the silicon—hydrogen distance, 1.576 Å, is the longest bond we have

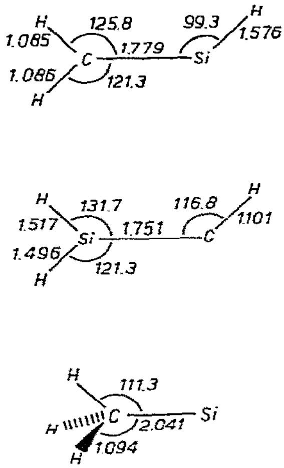

Fig. 2. Geometries of tautomers of $CSiH_3^-$ as optimised with the double-zeta basis set. Bond lengths are in Å and angles in degrees.

encountered between these two atoms. A third tautomer on this energy hypersurface, IX (C_{3v} symmetry), was also included as this structure, which minimises the amount of bonding between carbon and silicon, is at the lowest minimum on the corresponding cation surface [2]. The carbon—silicon bond length in IX, 2.041 Å, is longer than the same bond optimised for silaethane (1.903 Å [4]) and CH_3—Si^+ (1.860 Å [2]).

b) Relative energies of tautomers

3-Silapropyne is the most stable of the three tautomers examined on the C_2SiH_4 energy hypersurface at all three levels of theory (Tables 1 and 2). Relative to the double-zeta calculations, inclusion of *d*-orbitals on silicon increases the energy differences between tautomers but further improvement of the basis set by inclusion of *d*-orbitals on carbon and *p*-orbitals on hydrogen, while improving the total energies, does not change the relative energies significantly. Calculations on the four tautomers on the $C_2SiH_3^-$ hypersurface show a similar basis set dependence. On both hypersurfaces the tautomer in which the silicon is most saturated is the most stable, and increasing the unsaturation at silicon systematically raises the relative energy of the tautomers, in keeping with the previously noted tendency of silicon to avoid multiple bonds with carbon [1,2].

It is interesting to compare the relative stabilities of 1- and 2-silaallenes. It has previously been shown [5] that 2-silaallene is 45.7 kcal/mole above 3-silapropyne while our results show 1-silaallene to be higher by only 29.8 kcal/mole. Assuming that the calculations are of comparable quality then 1-silaallene is more stable than 2-silaallene by ~15 kcal/mole, thereby providing a further example of silicon avoiding multiple bonds with carbon.

In 1-silapropyne the silicon is formally involved in a triple bond with carbon and this unfavourable arrangement results in an energy 68.9 kcal/mole above 3-silapropyne. Nevertheless, 1-silapropyne is at a minimum on the surface, un-

TABLE 1

TOTAL ENERGIES (HARTREES) AT DOUBLE-ZETA OPTIMISED GEOMETRIES

Molecular species	double-zeta	double-zeta + *d*-orbitals on silicon	double-zeta + polarisation functions on all atoms
$H-C\equiv C-H$	−76.79909 [a]	—	—
$H-C\equiv C^-$	−76.17462 [b]	—	—
$H_2C=CH_2$	−78.01199 [c]	—	—
$H_2C=CH^-$	−77.32462 [b]	—	—
$H_3C-C\equiv C-H$	−115.8341 [d]	—	—
$H_2C=C=CH_2$	−115.83020	—	—
$H_3C-C\equiv C^-$	−115.19623	—	—
$H_2C=C=CH^-$	−115.1851 [d]	—	—
$H_2C=SiH^-$	−328.41844	—	—
$H_2Si=CH^-$	−328.33962	—	—
H_3C-Si^-	−328.37859	—	—
$H_3Si-C\equiv C-H$	−366.85250	−366.89964	−366.93151
$H_2C=C=SiH_2$	−366.81269	−366.85153	−366.88398
$H_3C-C\equiv Si-H$	−366.76153	−366.78802	−366.82173
$H_3Si-C\equiv C^-$	−366.25748	−366.30259	−366.33219
$H-C\equiv C-SiH_2{}^-$	−366.26144	−366.29157	−366.32306
$H_2C=C=SiH^-$	−366.24929	−366.27728	−366.30665
$H_3C-C\equiv Si^-$	−366.25357	−366.27541	−366.30472

[a] Experimental geometry used [30]. [b] Geometry as optimised with 4-31G basis set, reference 22. [c] Geometry optimised at double-zeta level; C—C 1.334 Å, C—H 1.075 Å and C—C—H = 121.8°. [d] Reference 25.

like silaacetylene for which there is no barrier to the 1,2-hydrogen shift to form the more stable vinylidenesilene [2].

On the $CSiH_3{}^-$ energy hypersurface silicon-deprotonated silaethylene (VII) is the most stable, 25.0 kcal/mole below IX, and 49.5 kcal/mole below carbon-deprotonated silaethylene (VIII). No attempt was made to study the profiles to interconversion of these three anions.

TABLE 2

RELATIVE ENERGIES (kcal/mole) OF TAUTOMERS OF C_2SiH_4 AND $C_2SiH_3{}^-$ AS A FUNCTION OF BASIS SET

	double-zeta	double-zeta + *d* on Si	double-zeta + polarisation functions on all atoms
a) Tautomers of C_2SiH_4			
$H_3SiC\equiv CH$	0	0	0
$H_2Si=C=CH_2$	25.0	30.2	29.8
$H_3C-C\equiv SiH$	57.1	70.1	68.9
b) Tautomers of $C_2SiH_3{}^-$			
$H_3SiC\equiv C^-$	0	0	0
$H-C\equiv C-SiH_2{}^-$	−2.5	6.9	5.7
$H_2C=C=SiH^-$	5.1	15.9	16.0
$H_3C-C\equiv Si^-$	2.5	17.1	17.2

c) Effect of silicon substitution on acidity

Theoretical acidities can be obtained by calculating the difference in energy between the Brønsted acids and their anions. This gives a measure of ΔE_0^0 for the deprotonation reaction given in equation 1. A small value of ΔE_0^0 indicates a high acidity.

$$AH \rightarrow A^- + H^+ \qquad (1)$$

For hydrocarbons the relative acidities of hydrogens is alkynyl > alkenyl > alkyl and the same trend in carbon acidity is maintained when a carbon atom is replaced by a silicon (Table 3). Assuming carbon deprotonation the double-zeta level calculations give silaethane to be more acidic than ethylene by 33.0 kcal/mole; silaethylene is more acidic than ethylene by 18.7 kcal/mole; 3-silapropyne is more acidic than propyne by 26.9 kcal/mole; 1-silaallene is more acidic than allene by 58.9 kcal/mole; and 1-silapropyne is more acidic than the methyl group of propyne by 85.9 kcal/mole. Deprotonation of silaethane, silaethylene and 3-silapropyne all produce anions with similar structures to those of the parent acids and the relatively small enhancement in acidity caused by the presence of a silicon atom results from hyperconjugative delocalisation of the charge onto the silyl and silylene groups. Deprotonation of 1-silaallene produces an anion V which is structurally very different from the acid form. At the highest level of theory (double-zeta + polarisation functions on all atoms) the silylene group of 1-silaallene has a charge of +0.397 *e* while in the anion the same group has a charge of −0.473 *e*, a change of 0.870 *e* in this group as a result of deprotonation. Hence the large structural change has the effect of transferring the negative charge of the anion from the carbon which loses the proton to the silicon atom, which is better able to accommodate the negative charge. Deprotonation of allene does not produce the analogous structural change [23].

Deprotonation of the methyl group of 1-silapropyne results in a decrease of 0.145 Å in the carbon—carbon bond and an increase of 0.167 Å in the carbon—silicon bond to produce a structure similar to that of 1-silaallene. The increase of 0.705 *e* in the charge on the silynyl group on formation of this anion indicates that most of the negative charge is on the silicon end of the molecule and supports the assignment of structure VI. Propyne has previously been found to undergo a similar structural rearrangement on removal of a proton from the methyl group [23].

TABLE 3

COMPARISON OF ACIDITIES (kcal/mole) OF C—H BONDS ADJACENT TO CARBON OR SILICON ATOMS, AS COMPUTED AT THE DOUBLE-ZETA LEVEL

Molecule	X = C	X = Si
$HC{\equiv}XH$	392.0	—
$H_2C{=}XH_2$	431.5	412.8
$H_3C{-}XH_3$	448.7	415.7
$H_3C{-}C{\equiv}XH$	407.4	321.5
$H_3X{-}C{\equiv}CH$	400.4	373.5
$H_2C{=}C{=}XH_2$	404.9	346.0

TABLE 4

RELATIVE ACIDITIES (kcal/mole) of Si—H AND C—H BONDS IN MOLECULES CONTAINING BOTH SILICON AND CARBON ATOMS

Molecule	Acidity of Si—H			Acidity of C—H		
	Double-zeta	Double-zeta + *d* on Si	Double-zeta + polarisation functions on all atoms	Double-zeta	Double-zeta + *d* on Si	Double-zeta + polarisation functions on all atoms
$H_2C{=}SiH_2$	363.4	—	—	412.8	—	—
$H_3C{-}SiH_3$	387.0	399.5	400.6	415.7	413.0	416.3
$H_3Si{-}C{\equiv}C{-}H$	371.0	381.7	381.9	373.5	374.8	376.2
$H_3C{-}C{\equiv}Si{-}H$	318.9	321.8	324.5	321.5	320.6	323.3
$H_2Si{=}C{=}CH_2$	353.7	360.5	362.4	346.0	351.5	352.1

In molecules containing both silicon and carbon, with the exception of 1-silaallene, deprotonation occurs preferentially at silicon according to the double-zeta level calculations (Table 4). However inclusion of *d*-orbitals on silicon decreases the acidity at silicon and has little effect on the acidity at carbon. We attribute the decrease in acidity at the silicon atom to a larger improvement in the wavefuntion of the acid relative to that of the anion due to a better description of the bonding around the silicon atom when *d*-orbitals are included. We have noted that such an improvement increases directly with the number of hydrogen atoms attached to silicon (Table 1). The absence of any marked change in the acidity at the carbon atom as a result of inclusion of *d*-orbitals indicates that $(p \rightarrow d)$ π-interaction is not an important stabilising factor in the anions. The enhancement in acidity endowed by an adjacent silicon atom is then best explained in terms of hyperconjugation. Calculations at the same level of theory also show the silylmethyl anion to be strongly stabilised by the silyl group even in the absence of *d*-orbitals [4] and here hyperconjugation rather than $(p \rightarrow d)$ π-interaction appears to be the stabilising factor.

Further refinement of the wavefuntions by inclusion of *d*-orbitals on carbon and *p*-orbitals on hydrogen does not markedly change the computed proton affinities over the (double-zeta + *d* on Si) basis set calculations and we therefore conclude that this basis set provides a wavefunction sufficiently close to the Hartree-Fock level to yield reliable proton affinities. Experimental proton affinities are not available for comparison for these silicon compounds but previous work with the Dunning basis set on carbanions CH_2X^- [25] has produced proton affinities which are slightly higher than the experimental values (approximately 20 kcal/mole too high in proton affinities of around 400 kcal/mole, with the discrepancy being largest for the smallest substituents). The calculations in Table 4 used a comparable basis set and would be expected to overestimate the proton affinities by a similar small amount.

An α-silicon atom increases the acidity at a carbon by a much smaller amount than a β-silicon atom in conjugation with the carbanion centre. In order to test the importance of conjugation we have examined the acidities of the acetylenic hydrogens in 1-butyne (X) and 4-sila-1-butyne (XI). Geometries for both these molecules and the anions formed by removal of the alkynyl

$H_3C{-}CH_2{-}C{\equiv}C{-}H$ (X) $\quad$ $H_3Si{-}CH_2{-}C{\equiv}C{-}H$ (XI)

protons were optimised at the STO-3G level [26] and are given in Fig. 3. The computed total energies along with those for 3-silapropyne and its anion, also optimised at the STO-3G level for comparative purposes, are given in Table 5. Computed acidities for these and for other alkynes taken from the literature [27] are also included in Table 5.

The acidities computed at the STO-3G level are, as is usual, too large by approximately 100 kcal/mole. The relative acidities, however, are in the same order as those calculated with the more extensive double-zeta basis set. Previous experimental [28,29] and theoretical [27] work has established that the methyl group decreases the acidity of the alkynyl proton relative to the parent acetylene, and the relative order of acidities for alkynes RC≡CH follows the order R = H > t-butyl > i-propyl > ethyl > methyl. From our results in Table 5 the silyl group is atypical in that it enhances the acidity of the alkynyl proton, while the 2-silaethyl group behaves similarly to the ethyl group in slightly decreasing the acidity relative to ethyne. Deprotonation of 3-silapropyne results in a change of 0.318 *e* in the net-charge on the silyl group while deprotonation of 4-sila-1-butyne produces a change of 0.264 *e* in the 2-silaethyl group (only 0.178 *e* in the silyl fragment). Hence in the deprotonation more of the negative charge is transferred into the substituent when the silyl group is in conjugation with the anion centre. However, once again this delocalisation of negative charge cannot be attributed to ($p \rightarrow d$) π-interaction since *d*-orbitals are not included in the STO-3G basis set used for these calculations.

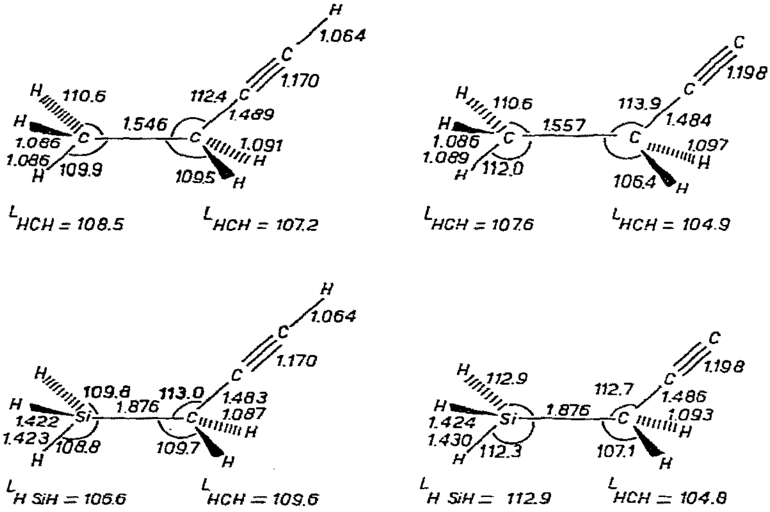

Fig. 3. Geometries of 1-butyne, 4-sila-1-butyne and the corresponding butynyl anions as optimised with the STO-3G basis set. Bond lengths are in Å and angles in degrees.

TABLE 5

TOTAL ENERGIES FROM STO-3G OPTIMISATION AND ACIDITIES

	Total energies (hartrees)	Acidities (kcal/mole)
$H_3SiC{\equiv}CH$	−362.66315	491.5
$H_3SiC{\equiv}C^-$	−361.88020	—
$H_3SiCH_2C{\equiv}CH$	−401.23546	497.7
$H_3SiCH_2C{\equiv}C^-$	−400.44261	—
$H_3CCH_2C{\equiv}CH$	−153.02883	497.0 (498.8) [a]
$H_3CCH_2C{\equiv}C^-$	−152.23710	—
$HC{\equiv}CH$	—	496.6 [a]
$CH_3C{\equiv}CH$	—	499.6 [a]

[a] Reference 27.

Conclusions

All three isomers of C_2SiH_4 examined here are at minima on the energy hypersurface but without studying profiles to their decomposition it is difficult to predict whether II and particularly III would be isolable. The orders of thermodynamic stability for both molecules C_2SiH_4 and anions $C_2SiH_3^-$ follow the order of saturation at silicon i.e. the structures which have the most hydrogens on silicon (or conversely the lowest bond order between carbon and silicon) are the most stable.

Silicon is more capable of sustaining a negative charge than carbon and, more important to synthetic chemistry where trimethylsilyl groups are frequently used, a conjugated silicon atom stabilises an adjacent carbanion centre. If, however, the silicon atom is not in conjugation with the carbanion centre, as in the 4-sila-1-butynyl anion, then it behaves rather like a carbon atom and is weakly destabilising. The stabilisation of a carbanion by silicon is not caused by π-delocalisation from the anion centre along the conjugated system to the *d*-orbitals of silicon since the ab initio calculations reproduce this stabilisation even in the absence of *d*-orbitals.

Both theory and experiment have shown the acidities of the methyl and alkynyl protons of propyne to be almost the same. Introduction of a silicon atom into either the 1 or 3 position of propyne has the effect of increasing the acidities of all the protons. Despite the greater intrinsic ability of silicon to carry a negative charge relative to carbon (as shown by the relative acidities of silane and methane) all the isomers of SiC_2H_4 are more easily deprotonated at carbon rather than at silicon. Hence in these molecules silicon appears to be even more effective at stabilising a negative charge when the charge is generated on an adjacent carbon atom. Such a generalisation does not extend to silaethylene and silaethane.

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