Tetrahedron, Vol. 37, pp. 1105 to 1112, 1981
Printed in Great Britain.

0040-4020/81/061105-08$02.00/0

A THEORETICAL INVESTIGATION OF α-SUBSTITUENTS ON THE STRUCTURE, PROTON AFFINITIES AND INVERSION BARRIERS OF SILYL ANIONS

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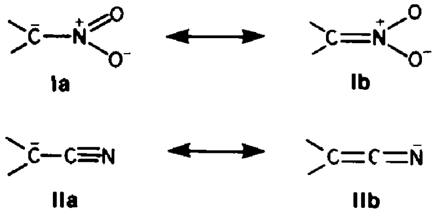
(*Received in USA* 16 *July* 1980)

Abstract—Geometries, optimised at the double-zeta level, are reported for silanes SiH_3X and silyl anions SiH_2X^-, where $X = H$, BH_2, CH_3, NH_2, OH and F. The anions are pyramidal with larger out-of-plane angles than their carbanion analogues and inversion barriers are large, varying from 34.3 kcal/mole for $X = H$ up to 57.3 kcal/mole when $X = F$. The silylborane anion is planar at both boron and silicon and has a Si–B bond length shorter by 0.15 Å than in silylborane. Silyl anions are more stable than methyl anions by between 55 and 66 kcal/mole.

In the last decade there have been many *ab initio* molecular orbital studies on substituent effects in molecules, radicals and in cations.[1-13] Many of these studies have employed minimal basis sets and anions, which are described much less satisfactorily with small basis sets, have not been examined in as much detail. Recently, however, extended basis sets have been used successfully to examine (a) the acidites of monosubstituted methanes,[14,15] primary amines,[16] and ketene, allene and ketenimine,[17] and (b) the effect of alkyl groups on acidities.[18]

Anions which have an electronegative substituent containing a double bond in conjugation with the anion centre, e.g.  $-C(=O)-R$, C≡N and NO_2 are particularly effective at stabilising carbanions, CH_2X^-, and amide anions, NHX^-. In these anions it is possible to draw classical valence bond structures (Ib and IIb) in which the negative charge is formally located on the heteroatom. If valence tautomers of the type Ib and IIb make large contributions to the structures of the anions then the C–X bonds (where X is the substituent) should be appreciably shorter in the anions than in the methanes. Such a decrease is, in fact, observed with the largest change (0.2 Å) being observed in the deprotonation of nitromethane.[14]


Ia Ib
IIa IIb

Theoretical studies show that conjugative stabilisation of the anions increases the acidity of methane by 65.3 kcal/mole for X=CHO, 55.3 kcal/mole for X=CN, and 91.6 kcal/mole for $X=NO_2$.[14] These results are in good agreement with gas phase experimental acidities.[19]†

Saturated electron-withdrawing groups ($X = NH_2$, OH and F) also increase the acidity of methanes CH_3X and amines NH_2X, but by much smaller amounts than the unsaturated substituents. For example the most effective of these substituents, F, only increases the acidity by 22.2 kcal/mole.[14] In saturated anions there are two conflicting interactions. Electron-withdrawal through the σ-bond by the electronegative element is the dominant interaction, but is partly offset by the 4π-electron destabilising interaction between the lone pairs on the substituent and lone pair at the anion centre.

Silicon, although more electropositive than carbon, is more capable of accomodating both positive and negative charges.[20,21] Recently Apeloig and Schleyer have used minimal basis set molecular orbital calculations to compare the relative effects of α-substituents on carbenium and silicenium ions.[13] Their work encouraged us to extend our studies on substituent effects in anions to monosubstituted-silyl anion, SiH_2X^-. Anions are not well described by minimal basis set calculations and we have therefore used the larger double-zeta basis set for geometry optimisations on both the silyl anions and their parent silanes, SiH_3X. Structures have not previously been reported for some of the molecules examined in this study. Both silanol ($X = OH$) and silylamine ($X = NH_2$) are unstable under laboratory conditions[22] but possibly exist in interstellar space.[23-25] Silylborane, a silane which is expected to be greatly destabilised by its strongly electron-withdrawing substituent, has not been observed experimentally. The parent silyl anion, SiH_3^-, is the only anion which has been extensively examined in the gas phase.[26]

Computational method. All calculations were for closed shell singlets. The primitive gaussian basis set used throughout 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.[27,28] For optimum structures the following polarisation functions[29] were used: d on Si 0.4; d on C 0.7; p on H attached to Si 0.433, and p on H attached to C 0.75. All geometry optimisations used the

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†There is no experimental value for the acidity of methane. However, there is good agreement between theory and experiment on the acidities of monosubstituted methanes.

gradient method[30,31] incorporated in the MONSTERGAUSS 80 program.[32]

RESULTS AND DISCUSSION

1. *Geometries*

(a) *Silanes.* Both experimental and theoretical[33] studies have established that the C–X bond lengths in monosubstitutedmethanes, CH_3X, decrease along the series $X = CH_3$, NH_2, OH and F. For the analogous silane series, SiH_3X, some of the compounds have not been isolated but from what experimental bond lengths are available (Si–F is 1.594 Å,[34] Si–C is 1.867 Å[35,36]) it would appear that there is the same trend. We now report geometries as optimised with the double-zeta basis set for the nolecules SiH_3X, where $X = BH_2$, CH_3, NH_2, OH and F (Fig. 1). As suggested from the limited experimental data there is indeed a monotonic decrease in the Si–X bond length along the series $X = BH_2$ to F. For fluorosilane and methylsilane the calculated bond lengths are too long by 0.09 Å and 0.036 Å respectively. Inclusion of d-orbitals on second row atoms, although not formally populated, permits (p→d) π-interaction and results in shorter bond lengths between neighbouring atoms[37] and it therefore seems probable that the Si–X bond lengths for silylamine and silanol given in Fig. 1 are a little too long.

In all the silanes the SiH_3 group is close to tetrahedral but the angles at the other "heavy" atoms are larger than the ideal angles. For example $<SiOH$ in silanol is 134.1°, as compared with 105.9° in methanol.[33] Similarly the experimental $<SiOSi$ of disiloxane, estimated at 145°[38] is considerably larger than $<COC$ (111.5°)[39] of dimethyl ether. In methylsilyl ether $<SiOC$ is 120.6°.[40] These large $<SiOX$ have often been explained in terms of (p→d) π-interaction between the lone pairs on the oxygen atom and the low-lying empty d-orbitals on silicon.[22] However, the double-zeta basis set employed in the optimisation does not include d-orbitals and such an explanation is therefore incorrect.

An alternative method of delocalising π-electron density from the substituent X onto the silyl group, through $X_\pi \rightarrow Si_\pi^*$ interaction, has been shown by a PMO study to be important in silaethane.[41] Examination of the coefficients of the highest-filled molecular orbitals of the other silanes showed large contributions from both the substituents X and the hydrogens of the silyl groups indicating that this interaction is also important in the other silanes.

In an attempt to assess the relevance of d-orbitals on Si to the geometry we carried out a partial geometry optimisation using a single set of d-orbitals on Si. The geometry of the silyl group was assumed to be unchanged by the additional functions and the optimisation, using the point-by-point parabola fitting method, was

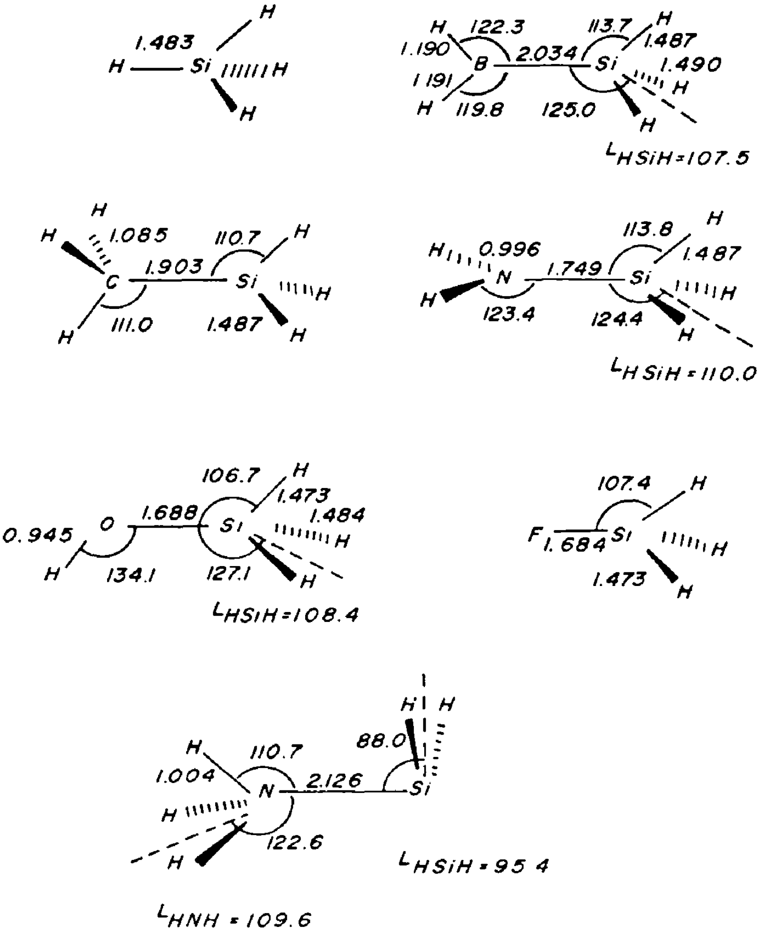
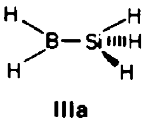


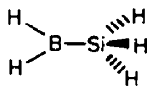
Fig. 1. Geometry as optimised with the double-zeta basis set for silanes SiH_3X. Bond lengths are in Å and angles in degrees.

focussed on the Si-O bond length and on <SiOH. The result of this optimisation was to *shorten* the bond by 0.05 Å, to increase the angle by 1.0°, and to improve the total energy by 0.001499 hartrees (0.9 kcal/mole). Inclusion of d-orbitals facilitates electron transfer from the OH group (there is a decrease of 0.164e in the (double-zeta + d) calculation over the double-zeta calculation) and the net-effect of permitting a $(p \rightarrow d)\pi$-interaction by inclusion of d-orbitals on Si is to shorten the Si-O bond length but to leave <SiOH essentially unchanged at its unusually high value of ~135.0°. These results and conclusions parallel previous calculations on the role of d-orbitals in the bonding in the 2-chloroethyl radical.[37]

In both silylamine and silylborane the substituents (NH_2 and BH_2) are planar. Both these molecules were subjected to geometry optimisations in the eclipsed IIIa and bisected IIIb conformations, and both were found to have no conformational preference. Silylborane is isoelectronic with the silylmethyl cation, in which there is also a negligible rotational barrier.[21]



IIIa

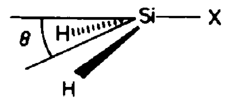


IIIb

In amines, substituents which are capable of acting as electron acceptors lower the energy of the lone pair on nitrogen and the N atom adopts a more planar arrangement than in ammonia, e.g. $(CH_3)_2N\ BCl_2$ is planar.[42] Similarly trisylamine, which has bulky silyl substituents which can act as electron acceptors, is planar at nitrogen.[43,44] No experimental geometry is available for silylamine but the molecular orbital calculations give this primary amine to be planar at nitrogen even in the absence of d-orbitals, thereby establishing that it is not necessary to invoke $(p \rightarrow d)\pi$-interaction to rationalise why the amine is planar at nitrogen.

Attempts to synthesise silylamine have been unsuccessful and, in general, both primary and secondary silylamines are unstable and tend to disproportionate.[22,45] Since silicon is able to accomodate a negative charge relatively easily and the amino group has a high proton affinity it seemed possible that the zwitterionic structure $H_2\overset{-}{Si}\overset{+}{N}H_3$ would be of similar energy to that of silylamine. We therefore performed a geometry optimisation on the zwitterion with the double-zeta basis set and found it to be *less* stable than silylamine by 24.7 kcal/mole (total energy = −346.19600 hartrees). Molecular orbital calculations are for isolated molecules at 0°K, and, since solvation stabilises ions relative to neutral molecules it seems possible that in solution at room temperature the zwitterion will be of similar stability to silylamine. There is, however, likely to be a high barrier to interconversion of these species as the 1,2-shift in the isoelectronic silylmethyl → methylsilyl anion rearrangement has a barrier of about 60 kcal/mole.[21]

(b) *Silyl anions.* Deprotonation of the silanes, SiH_3X, to produce the silyl anions, SiH_2X^-, results in an increase in the Si–X bond distance for the isoelectronic series X = CH_3, NH_2, OH and F (Fig. 2). A similar elongation is observed in the corresponding series of carbanions.[16] The out-of-plane angle, θ (see structure IV for a definition of θ), is also larger in the silyl anions than in the corresponding silanes.



IV

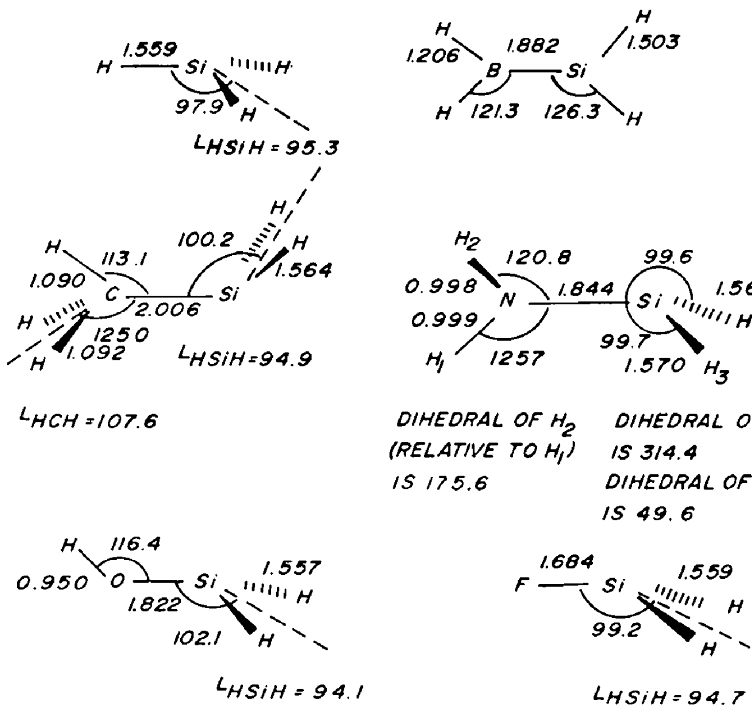
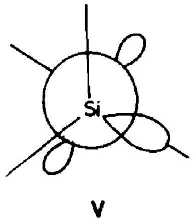


Fig. 2. Geometries as optimised with the double-zeta basis set for silyl anions, SiH_2X^-. Bond lengths are in Å and angles in degrees.

Both these structural changes are consistent with the SiH_2^- being a weaker electron acceptor than the SiH_3 group. In the silanes the $X_\pi \rightarrow Si_{\pi^*}$ interaction is significant and leads to a somewhat smaller Si–X bond length than might be expected. In the anions, however, π-donation from the substituent to the electron rich SiH_2^- group is less favourable and a 4π-electron destabilising effect is dominant. The effect on inversion barriers of lone pairs on a substituent attached directly to the atom about which inversion occurs has been studied in detail.[5,16,46] Both π-donation from the substituent (which interacts with the lone pair at the inversion centre to produce the 4π-electron destabilisation) and σ-withdrawal to the substituent increase the inversion barrier and produce an elongation of the bond to the substituent. In the four silyl anions SiH_2X^-, where $X = CH_3$, NH_2, OH and F, the substituents are all π-donors and σ-acceptors, and the anions all have larger inversion barriers than SiH_3^-, and the Si–X bonds are longer than in the corresponding silanes. In the silyl cations containing these same substituents π-donation from the substituent to the empty p-orbital on silicon is dominant and exactly the opposite behaviour, a shortening of the Si–X bond and a dimunition of θ (to zero) is observed.[13]

Silylborane, although perhaps less comparable since it has two fewer electrons, exhibits a *decrease* in Si–B bond length (by 0.152 Å) on removal of a proton. The anion is planar and therefore has the same structure as (but longer bond lengths than) the isoelectronic silaethylene.[47] In this anion, delocalisation of the lone pair from silicon to the slightly more electronegative and electron-deficient boron is sufficient to destroy the pyramidality of the Si atom.

The amino group of the silylamide anion is, as in silylamine, essentially planar at nitrogen, with $<SiNH$ also approximately the same size as in the acid form. The optimum conformation of the silylamide anion (structure V) is one in which the two adjacent lone pairs have maxima in orthogonal planes. This permits a maximum hyperconjugative interaction between the lone pairs and the H atoms on the adjacent atoms.



V

In the silanoxyl anion $<SiOH = 116.4°$, much closer to the value expected at oxygen than in silanol and all three H atoms eclipse lone pairs on the adjacent atoms.

2. *Relative stabilities of silyl and methyl anions*

The total energies for the silanes and silyl anions (listed in Table 1) can be used along with previously published data on carbanions[16] to calculate energies for the isodesmic reactions in eqns (1) and (2). Equation (1) permits assessment of the effect

$$SiH_2X^- + SiH_4 \rightarrow SiH_3^- + SiH_3X \qquad (1)$$

$$CH_2X^- + CH_4 \rightarrow CH_3^- + CH_3X \qquad (2)$$

of α-substituents in silyl anions and eqn (2) gives the effect in carbanions. The results in Table 2 show that, relative to hydrogen, the Me group is weakly destabilising in both silyl and Me anions, and the amino group destabilises the silyl anion but is weakly stabilising in the Me anion. Proceeding along the series $X = CH_3$ to F the substituents are progressively more stabilising, with the effect always being larger at carbon than at silicon. This higher dependence on the substituent for the methyl anions reflects the inability of carbon to accomodate a negative charge relative to silicon. The difference in these relative abilities is provided by eqn (3). The parent silyl anion is more stable than the Me anion by 65.8 kcal/mole.

$$SiH_2X^- + CH_4 \rightarrow SiH_3X + CH_2X^- \qquad (3)$$

The energy difference between the cations SiH_3^+ and CH_3^+ using eqn (3) for positive ions gives the silyl cation to be the more stable (by 50 kcal/mole experimentally[48] and 73.5 kcal/mole theoretically).[13]

Relative to carbon, ghen, silicon is better able to carry both positive and negative charges. In the anions, substituents reduce the difference in stabilities between silyl and Me anions, but the effect is less pronounced than in the corresponding cations.[13] In the cations the stabilisation derives mainly from π-donation from lone pairs on the hereoatoms into the formally empty p-orbitals of positively charged carbon or silicon atom. In the anions (except when X = H and BH_2) such an interaction is 4π-electron destabilising and electron-

Table 1. Total energies (hartrees) at double-zeta optimised structures for silanes and silyl anions

Substituent, X	H_3SiX		H_2SiX^-	
	Double-Zeta	Double-Zeta + d on Si	Double-Zeta	Double-Zeta + d on Si
H	-291.18071	-291.22695	-290.57412	-290.60217
BH_2	-316.42700	-316.45446	-315.83084	-315.85639
CH_3	-330.22093	-330.26764	-329.60435	-329.63121
NH_2	-346.23533	-346.29177	-345.61887	-345.65023
OH	-366.07619	-366.13971	-365.46956	-365.50430
F	-390.10087	-390.16596	-389.51378	-389.54965

Table 2. Calculated energies (kcal/mole) for eqns (1), (2) and (3)

Substituent, X	Equation 1	Equation 2	Equation 3
H	0.0	0.0	65.8
BH_2	15.6	---	---
CH_3	-6.2	-2.4	62.0
NH_2	-6.2	2.4	57.2
OH	0.0	14.2	51.6
F	12.30	22.2	55.9

withdrawal through the σ-bond is the only possible mechanism to remove electron density from the anion centre to the substituent. The charges on all the substituents in both the silanes and silyl anions are negative (Table 3), with the charge increasing in the sequence $BH_2 < H < CH_3 < NH_2 < OH < F$, the order of electronegativity,[49] for the silanes. All the anions have slightly larger negative charges than in the silanes and there is the same trend, except when $X = BH_2$ there is a dramatic increase in the charge on the substituent, a further indication of the importance of π-donation from the SiH_2^- group to the electron-deficient BH_2 group.

Inclusion of d-orbitals on silicon permits (p→d)π-interaction between the substituent and the silicon atom. This results in all substituents having less negative charge on the substituent, although they are all still negative. With the exception of the silylborane, the decrease in the charge on the substituent is larger for the silanes than for the corresponding anions. Hence (p→d)π-interaction is more important in the silanes than in the anions, where the silicon is already formally carrying a negative charge.

3. *Inversion barriers*

The silyl anions, with the exception of $BH_2SiH_2^-$ where π-donation dominates resulting in a planar anion, all have larger out-of-plane angles, θ, than their carbon analogues. Geometry optimisations on all the anions constrained to be planar at silicon permitted calculation of the inversion barriers (listed in Table 4). All the barriers are much larger than those of their carbon analogues.[16]. In this respect the calculations agree with the experimental observation that inversion in silyl anions has a lower limit of 24 kcal/mole.[50] In the only previous theoretical treatment on SiH_3^- the barrier was predicted to be 39.6 kcal/mole.[51]

In both the Me and silyl anions the out-of-plane angles increase with the electronegativity of the substituent. A

Table 3. Charges on substituents in silanes and silyl anions using different basis sets

	Acids	Difference in charge on substituent in acid and anion	Anions
	$H-SiH_3$		$H-SiH_2$
DZ	-0.170	0.108	-0.278
DZ + d	-0.098	0.114	-0.212
DZ + pol	-0.232	0.083	-0.315
	H_2B-SiH_3		H_2B-SiH_2
DZ	-0.129	0.591	-0.720
DZ + d	-0.062	0.585	-0.647
	H_3C-SiH_3		H_3C-SiH_2
DZ	-0.369	0.199	-0.568
DZ + d	-0.282	0.207	-0.489
DZ + pol	-0.306	0.190	-0.496
	H_2N-SiH_3		H_2N-SiH_2
DZ	-0.522	0.101	-0.653
DZ + d	-0.372	0.156	-0.528
	$HO-SiH_3$		$HO-SiH_2$
DZ	-0.594	0.082	-0.676
DZ + d	-0.430	0.142	-0.572
	$F-SiH_3$		$F-SiH_2$
DZ	-0.648	0.095	-0.743
DZ + d	-0.522	0.137	-0.659

Table 4. Proton affinities and inversion barriers (both in kcal/mole) and out-of-plane angles (in degrees) for SiH_2X^- and CH_2X^-

	Silicon			Carbon[(a)]		
Substituents (X)	Proton Affinity[(c)]	Inversion Barrier	$\Theta^{(b)}$	Proton Affinity[(c)]	Inversion Barrier	$\Theta^{(b)}$
H	380.8	34.3	82.1	446.6	8.1	66.7
BH_2	365.2	0.0	0.0	—	—	—
CH_3	387.0	40.4	79.8	449.0	8.1	59.2
NH_2	387.0	42.8	76.2	444.2	10.1	61.7
OH	380.8	50.7	77.9	432.4	20.4	70.7
F	368.5	57.3	80.8	424.4	23.7	75.2

(a) Data taken from reference 16.

(b) Out-of-plane angle Θ is defined in structure IV in text.

(c) The computed proton affinities are differences in electronic energies and do not include corrections for vibrational, rotational and translational energies.

molecular orbital rationalisation of this behaviour in terms of the σ-inductive effective and Π-conjugative effect is already available in the literature.[5,16,46]

The inversion barriers of the Me anion and the isoelectronic ammonia have been widely investigated theoretically.[52] In both species minimal basis set calculations overestimate the barriers, extended sp basis sets give low values, polarisation functions increase the barrier above the extended basis set result, and inclusion of correlation energy is unimportant. The addition of diffuse functions, which makes a "significant" decrease in the inversion barrier, are the only additional functions which we have not included in our study of the barriers of SiH_3 and $CH_3SiH_2^-$. The double-zeta basis set used in the geometry optimisations is of intermediate size and, judging by the slight overestimation of the barrier for CH_3^-, falls somewhere between the minimal and extended basis sets reported in the literature.[52] Addition of polarisation functions (d-orbitals on C and Si, and p-orbitals on H) results in only slight increases in the barriers (for total energies see Table 5). For SiH_3^- with d-orbitals only on Si, the barrier is 37.0 kcal/mole, and with all the polarisation functions the barrier is 36.0 kcal/mole. For $CH_3SiH_2^-$ with only d-orbitals on Si the barrier is 42.9 kcal/mole, and with all the polarisation functions the barrier is 41.5 kcal/mole. From these results we conclude that the theoretical inversion barriers for silyl anions in Table 4 are probably slightly too high but there is no doubt that inversion barriers at silicon are large and much higher than in the analogous carbanions.

4. *The effect of polarisation functions*

Inclusion of polarisation functions is costly and it is economically important to determine which experimental features can be reproduced without their inclusion. In determining geometries the silyl group is well described and the large bond angles at SiOH and SiNH are reproduced without inclusion of any polarisation functions. However, the double-zeta basis set gives bond lengths Si–X which are slightly too long and this, according to the partial optimisation on silanol, can be rectified by inclusion of only d-orbitals on silicon. The experimentally high barriers to inversion at silicon are reproduced with the double-zeta basis set and inclusion of d-orbitals on silicon and polarisation functions on all atoms does not significantly change the calculated barrier. Inclusion of d-orbitals on silicon improves the wavefunctions of the silanes more than those of the anions, due to the higher importance of $(p \rightarrow d)\pi$-stabilisation in the silanes and also a better description of the bonding between Si and H, and this results in an increase in the computed proton affinities of the anions when d-orbitals are included. The proton affinities are not changed significantly by a further improvement of the wavefunction by including polarisation functions on carbon and hydrogen.

Intuitively we expected the d-orbitals on silicon to be the most important polarisation functions and for all the species in Table 5 this appears to be true. However it is possible that a similar improvement would be made by the first polarisation functions added to the double-zeta basis set regardless of their location, and in order to check this possibility we performed a calculation on $CH_3SiH_2^-$ in which only the carbon atom had d-orbitals. The energy obtained, −329.61720 hartrees, is only 8.1 kcal/mole better than the double-zeta calculation, as compared with an improvement of 16.9 kcal/mole when d-orbitals are used on only silicon. In this anion the d-orbitals on carbon are potentially useful in delocalising the negative charge onto the substituent Me group whereas the d-orbitals on silicon are not useful in delocalising the charge. Nevertheless the silicon orbitals are the more important.

In conclusion, most structural properties and substituent effects in silanes and their anions can ge obtained by use of double-zeta basis set molecular orbital calculations. However, for some features inclusion of d-orbitals is desirable.

Acknowledgements—We thank the Natural Science and Engineering Research Council of Canada for financial support and York University Computer Centre for generous allotments of computer time.

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Table 5. Effect of polarisation functions on total energies (hartrees) and proton affinities (kcal/mole) of SiH_3^- and $CH_3SiH_2^-$

		Double-Zeta	Double-Zeta + d on Si	Double-Zeta + polarisation functions on all atoms
SiH_4	Energy	-291.18071	-291.22695	-291.23388
SiH_3^-	Energy	-290.57412	-290.60217	-290.60600
	Proton Affinity	380.8	392.2	394.1
CH_3SiH_3	Energy	-330.22093	-330.26764	-330.28959
$CH_3SiH_2^-$	Energy	-329.60435	-329.63121	-329.65147
	Proton Affinity	387.0	399.5	400.6

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