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SUBSTITUENT EFFECTS IN SECOND ROW MOLECULES

SILICON-CONTAINING COMPOUNDS

ERIC MAGNUSSON
Contribution from the Research School of Chemistry, Australian National University,
G.P.O. Box 4, Canberra, A.C.T., Australia 2601

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Abstract - Substituent interaction energies are calculated by *ab initio* molecular orbital methods for the two series SiH_2X^- and SiH_3X for the directly bound substituents X = BH_2, CH_3, NH_2, OH, F and the results compared with those for the corresponding first row species. Interactions with the groups NH_2, OH, F are as large in the neutral as in the anionic series and this is attributed to the presence of important π-bonding interactions, supplementing the effects of inductive withdrawal of σ-electrons. The restoration of charge neutrality by π-donation to silicon is more important in the neutral molecules, σ-electron transfer from silicon in the anions. π-Bonding with the π-acceptor substitutent BH_2 is favourable, as it is in the CH_3X and CH_2X^- systems, but with π-donor substituents the interactions are always destabilizing.

Substituent effects in first row hydrides, including the neutral and anionic carbon-containing species, have been systematically studied by *ab initio* molecular orbital methods and the results rationalized by perturbation theory arguments, chiefly at the hands of Radom and co-workers.[1] The substituent interaction energy approach used by them is now extended to substituted second row compounds. The silicon-containing series SiH_3X and SiH_2X^- are treated here, similar results on phosphorus- and sulfur-containing species being reported in separate publications.[2]

Although the last word has yet to be said, the chemical literature is rich with comparative treatments of carbon and silicon.[3] There is consensus that some of the contrasts in substitution behaviour result from (a) the very strong bonding between silicon and very electronegative elements, and (b) the weakness of π-interactions, mainly because the bonds are long.[4] *d* orbitals are frequently invoked to explain unusual features but other explanations, such as hyperconjugation, are just as effective.[3b]

Theoretical substituent parameters for the SiH_3 and SiH_2^- groups, obtained by Topsom's procedures,[1c] offer a convenient means of describing the characteristics of the second row groups and comparing them with other species. Values for these groups and for CH_3[1c] are:

Species:	SiH_3	SiH_2	CH_3
σ_X(theor.)	−0.17	−0.26	0.17
σ_F(theor.)	−0.06	−1.94	−0.02
σ_R(theor.)	0.04	−0.19	−0.03

METHOD OF CALCULATION

Geometry optimization by the gradient method for the two series of silicon-containing compounds was carried out with the Gaussian 80 series of programs[5] at the restricted Hartree–Fock, single determinant, level. The supplemented 3-21G basis set was used.[6] Single point calculations at the 3-21G(#) geometries were then obtained at the 6-31G# # basis set level.[6] Calculations on the SiH_2X^- series compounds were repeated with an extra set of diffuse *s* and *p* functions in the basis set as recommended by Spitznagel *et al.* for work on anions (the 6-31 + G# # set).[7] Preliminary calculations suggested the value k = 0.04 for the exponent of the diffuse functions. The CH_2X^- series compounds were also recalculated with a basis set containing diffuse functions (4-31 + G).[7]

Detailed population analysis data for the silicon series compounds are reported in a paper devoted to bonding in second row molecules. As shown elsewhere,[2] the σ and π components of density matrix data are relatively insensitive to basis set variation with the standardized "Gaussian" basis sets and, when used cautiously, are valuable in predicting the trends in bonding in substitution series like SiH_3X and SiH_2X^-.

RESULTS

Energies and optimized geometrical data for the SiH_3X and SiH_2X^- series (X = H, BH_2, CH_3, NH_2, OH, F) are reported in Fig. 1 and Table 1. Substituent interaction energies appear in Table 2 and acidities, calculated relative to the acidity of parent hydride SiH_4, in Table 3.

The quality of the predictions of structure made by geometry optimization methods at various basis set levels has been pronounced upon elsewhere.[3a] Deviations from experimentally determined structures are generally fairly small.[3a] The almost planar geometry around nitrogen in $SiH_3 \cdot NH_2$ has been attributed by Hendewerk *et al.*, to the "bias of double-zeta basis sets to planar structures".[3a] The potential well associated with pyramidalization is not deep and such bias as exists is not expected to have much effect on relative energy results.

Bond lengths, as estimated by optimization, are up to 10 pm shorter in the neutral compounds than in the anions. The X = BH_2 case is the exception, where the Si lone pair is used effectively in π-bonding (calculated π-bond order 0.47, bond shortening relative to the Si—B bond in the neutral compound $SiH_3 \cdot BH_2$ 18 pm). Although the additional pair of electrons present in the almost iso-structural NH_2-substituted compounds would be expected to lead to repulsive interactions in the π-system, the π-orbital interactions are stabilizing. Presumably the heavy withdrawal of σ-electrons by

Table 1. Calculated total energies (Hartrees) of SiH_3X and SiH_2X^- series molecules ($X = H, BH_2, CH_3, NH_2, OH, F$)

SiH_3X:	Basis set:	3-21G(#)	6-31G # #
X = H		−289.73572	−291.23009
BH_2		−314.82785	−316.46752
CH_3		−328.57488	−330.28039
NH_2		−344.50841	−346.29482
OH		−364.24680	−366.13919
F		−388.14517	−390.14948

SiH_2X^-:	Basis set:	3-21G(#)	6-31G # #	6-31 + G # #
X = H		−289.11441	−290.60891	−290.61795
BH_2		314.22960	−315.86701	−315.87671
CH_3		−327.94054	−329.64822	−329.65742
NH_2		−343.86254	−345.65448	345.57323
OH		−363.60144	−365.50171	−365.52365
F		−387.51547	−389.52486	−389.54660

Table 2. Calculated interaction energies (kJ mol^{-1}) for SiH_3X, CH_3X, SiH_2X^- and CH_2X^- series molecules ($X = BH_2, CH_3, NH_2, OH, F$).[a]

	SiH_3X		CH_3X
Basis set:	6-31G # #	3-21G(#)	4-31G
X = BH_2	−61.5	−58.3	37.3
CH_3	−51.1	−38.8	−97.7
NH_2	3.4	61.6	−127.1
OH	48.3	126.3	−132.6
F	106.2	189.5	−110.4

		SiH_2X		CH_2X^-	
Basis set:	6-31 + G # #	6-31G # #	3-21G(#)	4-31 + G	4-31G
X = BH_2	−5.5	−7.2	2.2	207.2	245.5
CH_3	−79.6	−80.0	−73.0	−112.6	−88.8
NH_2	−21.5	−46.9	−2.9	−116.5	−105.4
OH	39.4	5.5	63.1	−72.9	−66.8
F	130.5	97.1	167.5	−5.6	−7.7

[a] All calculations on 3-21G(#) optimized geometries. 4-31G level results on carbon compounds from Pross *et al.*[1] Interaction energies refer to the processes:

$$SiH_3X + H_2 \rightarrow SiH_4 + HX, \text{ etc.}$$

Table 3. Calculated relative acidities (kJ mol^{-1}) of SiH_3X and CH_3X series Molecules.[a]

	SiH_3X			CH_3X	
Basis set:	6-31 + G # #	6-31G # #	3-21G(#)	4-31 + G	4-31G
X = BH_2	56.0	54.3	60.5	244.5	282.9
CH_3	−28.4	−28.9	−4.23	−14.9	−8.9
NH_2	−24.8	−50.3	−64.5	10.6	21.7
OH	−8.9	−42.8	−63.2	59.7	65.8
F	24.3	−9.0	−22.0	104.9	102.8

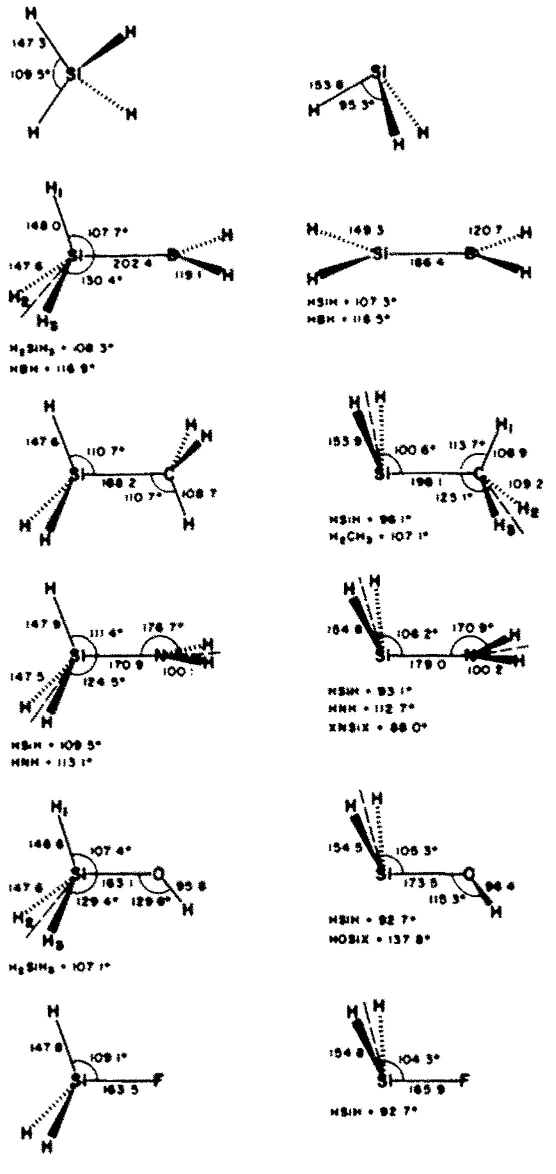

Fig. 1. Optimized geometries for SiH_3X and SiH_2X^- series molecules ($X = H, BH_2, CH_3, NH_2, OH, F$) obtained from 3-21G(#) level calculations. (Bond lengths in pm, bond angles in degrees.)

nitrogen allows for an effective role for σ-electrons in restoring charge neutrality. Although repulsive interactions are minimized in the anion by a conformation in which the dihedral angle between the SiH_2 and NH_2 bisectors is close to 90°, there is a bonding π-interaction even in the anion. Because it is smaller (Si—N bond order 0.12 in $SiH_2 \cdot NH_2^-$ compared with 0.22 in $SiH_3 \cdot NH_2$), there is a bond lengthening of 8 pm. The situation with the compounds of the other π-donor substituents, OH and F, is similar.

As also found for the sulfur and phosphorus series,[2] there are sizeable differences between substituent interaction energies calculated at the split valence basis level 3-21G(#) and the higher level 6-31G## basis. The differences do not obscure the trends evident in the higher level results and, as expected, they are quite small in the case of the relative acidity values which, because the proton exchange process is isodesmic,[8] allows a more effective cancellation of the errors retained in *ab initio* energy calculations at the single determinant level.

Proton affinities calculated for the anions SiH_3^- and $SiH_2 \cdot CH_3^-$ lie close to those calculated by Hendewerk *et al.*, with the larger basis set (including supplementation).[3a]

DISCUSSION

Relative energy calculations show the interaction between silicon and substituents NH_2, OH, F to increase strongly across the sequence, equally so for both the SiH_3X and SiH_2X^- series. This is unexpected, because the charged molecules would be expected to be rather more sensitive than the neutrals to charge transfer, whether to silicon or from it. The fact that the stabilizing trend in the analogous carbon compounds was larger for the charged CH_2X^- series than for the uncharged CH_3X compounds was used by Pross *et al.*, to suggest that a stabilizing inductive withdrawal in the σ-bond system of the negatively charged molecules was mainly responsible.[1b] The interaction energy and population data suggest the same powerful σ-electron withdrawal in the silicon compounds. However, σ-bonding in the 2nd row compounds is supplemented by unexpectedly strong π-interactions, especially in the neutral SiH_3X series, the net effect of which is to produce practically identical responses to NH_2, OH, and F in the two series.

The bond order data (included in Fig. 2) for these series show strong π-bond contributions to the Si—X

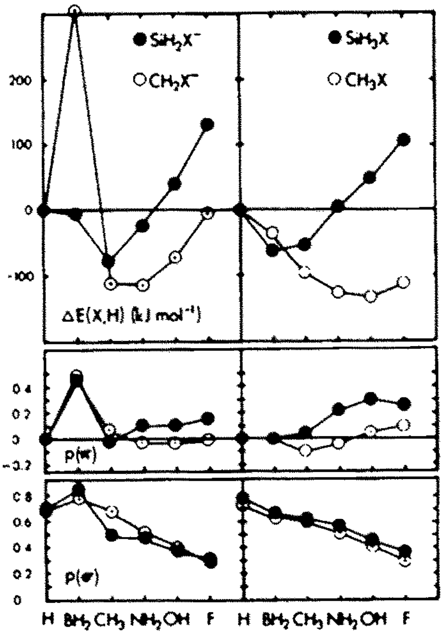

Fig. 2. SiH_3X and SiH_2X^- substituent interaction energies (kJ mol^{-1}; from 6-31G## and 6-31+G## level calculations) and calculated σ- and π-bond orders (from 3-21G(#) level calculations). All calculations on geometries optimized at 3-21G(#) level. Included for comparison are data for the corresponding first row CH_3X and CH_2X^- series compounds (open circles; energy data from refs 1 and 7).

bond orders for both series of compounds. Although the π-bond orders are smaller in the SiH_2X series, where interaction between the lone pairs of X and SiH_2 would not generally be expected to be favourable, they are still large, both the $p\pi$- and $d\pi$-orbitals making significant contributions to the final result. However, the population data also show how strongly the more electronegative substituents withdraw charge from silicon, particularly in the anions. The gross atomic population of the silicon $3p$ orbitals ranges from 2.1–1.9 for the SiH_3X series; in spite of the extra charge, the atomic populations rise to no more than 2.6–2.3 in the negatively charged SiH_2X^- series. In this situation charge transfer from substituent X to silicon in the π-system is an important means of restoring charge neutrality. π-Bonding is robust and only the methyl-substituted member of the anionic series exhibits an anti-bonding π-component of the Si—C bond.

The nature of the increase in the π-component of the Si—X bond order across the two series is noteworthy, because of the unexpected importance of this component of the bond for X = NH_2, OH, F. This may be explained by the nature of the interactions across the series. The second row element is not presented with a single $p\pi$-orbital as it would be, for example, when bound to the phenyl group. Inspection of the population data for these compounds shows that the $NH_2\cdot$ group employs one $p\pi$-orbital ($SiNH_2$ is almost planar in both series), the OH group presents two (one partly involved in the OH bond), and the fluorine atom employs both its $p\pi$ lone pairs. The interaction, correspondingly, increases from NH_2 to F.

Looking at the energy and population data as a whole, it seems that the effect of π-bonding stabilizes the P—X bond (strongly in the SiH_3X series and only slightly less strongly in the SiH_2X^- series), silicon p-orbital populations being so low. Added to the effect of σ withdrawal in bonds to N, O, and F, which is expected to stabilize the anions more than the neutrals, π-bonding keeps the results for the two series parallel. Because they are so parallel, the acidity results for the SiH_3X series vary very little. In CH_3X, where π-bonding is not sufficient to offset the large advantage to CH_2X by electron withdrawal, the acidities drop very quickly from X = NH_2 to F.

Binding to the π-acceptor BH_2 produces an entirely predictable result of a stabilization of the anionic species which almost disappears in the neutral compound, $SiH_3\cdot BH_2$. The stabilization is much less strong than in the analogous first row compound.

The effect of including d functions in calculations of second row molecules has been discussed elsewhere.[9] Hendewerk *et al.*[3a] conclude from comparisons of results from d function supplemented and unsupplemented basis sets that the d functions make only a marginal difference to the wave functions (significant when accurate estimates of, say, proton affinities are sought) and that other concepts are more important in explaining many experimental results. They conclude that the CH_3/SiH_2^- stabilization is hyperconjugative and not dependent on $p\pi$–$d\pi$ interaction. Results from these calculations are in agreement with this claim, but it should be noted that the π-interaction between carbon and silicon is the weakest of the substituent interactions studied here and that both σ- and π-bonding are much stronger with the substituents NH_2, OH and F than they are with CH_3.

CONCLUSIONS

A strong increase in substituent interaction between silicon and the σ-acceptor groups NH_2, OH, F is calculated for both the neutral and anionic series SiH_3X and SiH_2X^-. This contrasts with the first row systems CH_3X and CH_2X^-, where the progressive stabilization of the anions far exceeds that of the neutral compounds, as expected if inductive withdrawal of σ-electrons is the dominant interaction. The second row data are rationalized on the basis of the strong π-interactions calculated for the second row molecules, π-bonding being stronger in the neutral series where the σ-electron donor–acceptor interactions are apt to be weaker.

Although the calculated interaction energies are consistent with the notion that multiple bonding is weaker in second row molecules than in their first row analogues (as witness the lower stabilization calculated for the π-acceptor BH_2 with SiH_2^- than with CH_2^-), there is an important role for partial π-bonding to electronegative elements. Charge equalization by this means appears to make an important contribution to the high strength of the Si—O and Si—F bonds.

The differences between first and second row molecules are very clearly seen in the acidity data where, for the reasons just given, the trends are in opposite directions.

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[6a] As used in this paper, the supplemented basis sets designated 3-21G(#) and 6-31G # # contain five d functions rather than the six recommended by the Pople group. The absence of what is equivalent to an additional s function facilitates comparison of supplemented and unsupplemented basis set results. There is no significant difference between the performance of the two basis sets other than slightly higher energies for the six d function set. [b] As found in calculations of P and S, electron populations of Si in compounds containing O and F suffer from an excessive concentration of electron density in the poorly described outer components of the split valence functions. This feature is not present in the 6-31G # # level calculations.

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