Anomeric Effects Involving Silicon Centres: Silanols

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Ab initio calculations at the HF/6-31G* (and in some cases MP2/6-31G*)//3-21G(*) level on $H_{4-n}Si(OH)_n(n = 0$—4) species show that significant anomeric (negative hyperconjugation) stabilizations occur at silicon centres; in contrast, π-bonding with silicon 3d orbitals is a minor effect.

The influence of the anomeric effect on energies and conformational preferences of organic compounds with geminal electronegative substituents is now well established.[1] The underlying cause, 'negative hyperconjugation'[2,3] also has been postulated to be involved in systems with central atoms other than carbon, e.g. sulphur, phosphorus,[1a,3b,3c] and boron.[4]

There is increasing evidence that negative hyperconjugation operates in silicon compounds as well.[3b,5—14] The stabilization of α-silyl carbanions,[5] planarity at nitrogen and reduced Si–N bond lengths in silylamines,[6] the nearly linear SiNSi bond angle in $R_2Si=N–SiR_3$,[11a,c] the linear correlation of angle widening with decrease in Si–O bond lengths in siloxanes,[7] some of the remarkable properties of cyclopolysilanes,[8] and unusual structural features of 4-membered rings containing OSiO and NSiN units[9] can be attributed at least in part to this effect. Furthermore, the most electronegative substituent at silicon in substituted silylamines is generally oriented anti, if not parallel, to the nitrogen lone pair.[10] For chlorosilyl-N,N-dimethylamine, this conformational preference is also accompanied by remarkable bond lengths, short for Si–N and long for Si–Cl.[10c] Hyperconjugation (no-bond resonance) has been implicated[11a] to occur in silaethene[11b] and in silanimine[11c] Lewis base adducts; for instance, in the adduct of fluoride ion with a substituted silaethene,[11b] the original Si=C bond is

twisted by 90° and the FSiCR̄$_2$ unit is roughly coplanar, and $p_\pi(C) \rightarrow 2\sigma^*(Si–C)$ hyperconjugation can be postulated.

$(SiH_2Me)_2O$ has a conformation[14] that is nearly ideal for hyperconjugation, with $p_\pi(O) \rightarrow \sigma^*(Si–C)$ dihedral angles of 30°. Negative hyperconjugation should be especially significant for silicates owing to the presence of multiple O–Si–O units. The large Si–O–Si angles observed in silyl ethers,[14] siloxanes,[7] and silicates (average value, 149°)[15] have been attributed to Si–O π-bonding in addition to ionic contributions.[16] The average Si–O bond length (1.63 Å) in siloxanes is markedly shorter than the covalent radii sum (1.84 Å), and even shorter than the value estimated (1.69 Å) when corrected for ionic contributions.[3b,17]

Although $(d-p)_\pi$ bonding[6,10b,10c,18] is the most widespread hypothesis to explain the π-acceptor properties of silicon, there is increasing evidence that this factor is relatively unimportant.[19] Simple electronegativity arguments have also been advanced to explain the bond lengths and angles in silicon species,[12,16,17b,19] but negative hyperconjugation has been proposed much less often.[5,16,19d]

We have studied the O–Si–O anomeric effect at silicon centres by carrying out ab initio HF/6-31G*//HF/3-21G(*) calculations[20] on the series of molecules $H_{4-n}A(OH)_n(A = C,$ Si; $n = 0$—4). For molecules with $n = 0$—2, additional

Table 1. Selected geometrical parameters (Å, degrees), absolute energies (a.u.), energies for the group separation reaction (1) (kcal/mol), and relative energies for $H_{4-n}A(OH)_n$, at the ab initio HF/6-31G*//HF/3-21G(*) level.[a]

Species	Sym.	R(A–O)	R(A–H)	θ(HSiO)	θ(OSiO)	E	ΔE(1)[b]	ΔE$_{rel}$
H_4C[c]	T_d		1.083			−40.19517		
H_3COH[c]	C_s	1.440	1.085, 1.079	112.3(2), 106.3		−115.03378		
$H_2C(OH)_2$	C_s	1.420	1.085, 1.072	110.4(2), 105.8(2)	114.4	−189.89174	12.14 (13.63)[a]	3.73 (3.79)[a]
$H_2C(OH)_2$[c]	C_2	1.420	1.078	112.2(2), 105.1(2)	112.4	−189.89768	15.78 (17.42)[a] [17.4][a]	0.00 (0.00)[a] [0.0][a]
$HC(OH)_3$	C_3	1.408	1.072	110.1	108.8	−264.76664	19.04	
$C(OH)_4$	D_2	1.389			112.1(4), 104.3(2)	−339.64323	23.83	2.38
$C(OH)_4$	S_4	1.388			114.2(2), 107.2(4)	−339.64703	26.22	0.00
H_4Si[c]	T_d		1.487			−291.22492		
H_3SiOH[c]	C_s	1.633	1.478, 1.468	112.1(2), 107.3		−366.12898		
$H_2Si(OH)_2$	C_2	1.627	1.480, 1.459	111.7(2), 105.2(2)	112.2	−441.04232	5.82 (7.26)[a] [9.2][a]	1.95 (2.16)[a] [2.0][a]
$H_2Si(OH)_2$	C_s	1.630	1.468	109.3(2), 107.1(2)	113.1	−441.04542	7.77 (9.42)[a] [11.2][a]	0.00 (0.00)[a] [0.0][a]
$HSi(OH)_3$	C_3	1.625	1.458	110.1	108.8	−515.96468	9.54	
$Si(OH)_4$	D_2	1.621			111.8(4), 104.8(2)	−590.88144	7.97	3.84
$Si(OH)_4$	S_4	1.620			114.2(2), 107.1(4)	−590.88756	11.81	0.00

[a] Values in parentheses are at MP2/6-31G*//HF/3-21G(*); values in square brackets are at HF/3-21G//HF/3-21G. [b] Energy for bond separation reaction (1). [c] HF/3-21G(*) geometry taken from R. Whiteside, M. J. Frisch, and J. A. Pople, 'The Carnegie-Mellon Quantum Chemistry Archive,' Pittsburgh, 1983.
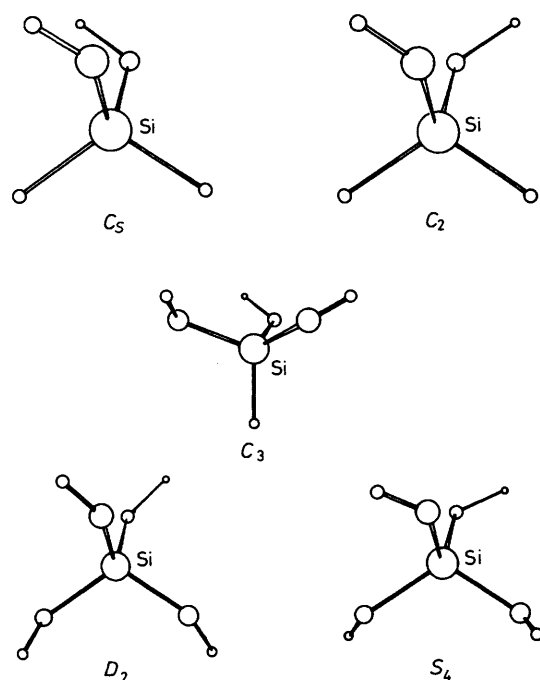
Figure 1. Optimized 3-21G(*) structures of the C_s and C_2 conformers of $H_2Si(OH)_2$, the C_3 conformer of $HSi(OH)_3$, and the D_2 and S_4 conformers of $Si(OH)_4$.

HF/3-21G//HF/3-21G and MP2/6-31G*//HF/3-21G(*) calculations[20] were performed to probe the importance of d orbitals on silicon and of electron correlation, respectively.

In the most stable conformers, the OH bonds are always roughly perpendicular to the vicinal A–O bonds (Figure 1). The best structures benefit from more favourable *anti* orientations of the OH bond-dipoles as well.[2,19a] For example, the C_2 and C_s conformations of the diols are equivalent with respect to negative hyperconjugation, but dipole orientations favour the former.[2,19a] Similarly, the S_4 form of the tetrahydroxy species is more stable than the D_2 conformation owing to the better orientation of the OH bond dipoles in the former (Figure 1). The conformational preferences are qualitatively similar for silanols and their anomeric carbon analogues.
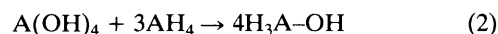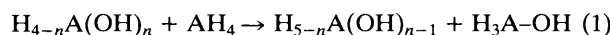
The calculated geometries are in good agreement with available experimental data on carbon compounds. While many results for $H_2C(OR)_2$ are available,[1,2] structural information on species with more oxygen substituents are sparse. For $C(OMe)_4$, electron diffraction shows an S_4 structure to be favoured.[21] Numerous crystal structures of silane diols[22] and triols[23] are available, but extensive intermolecular hydrogen bonding precludes even a qualitative comparison between the calculated and observed conformations.[22] However, for $Me_2(HO)Si–O–Si(OH)Me_2$, i.r. studies reveal one of the O–Si–O–Si dihedral angles to be about 70° (90° would be 'ideal').[24]

Note from Table 1 that the A–O bond length contraction with increasing OH substitution is much less for silicon than for carbon; the corresponding fluorine-substituted systems behave similarly.[3b] The Si–O bond lengths in Me_3SiOMe and in $MeSi(OMe)_3$ determined by electron diffraction are nearly the same, at 1.639 ± 0.004 and 1.632 ± 0.004 Å, respectively.[19a] This small contraction of 0.007 ± 0.008 Å [consistent with the corresponding difference of 0.008 Å between H_3SiOH and $HSi(OH)_3$ in Table 1] has been taken as evidence that a significant anomeric effect does not occur in $RSi(OH)_3$

species.[19a] However, this is not a valid argument, because negative hyperconjugation in species such as $H_{4-n}AY_n$ (Y = OH, F, *etc.*) is *bidirectional* and contributes not only π-bonding but also σ-antibonding character to the A–Y bonds.[3b] Analysis of the fluoromethane series indicates that A–Y bond contraction in such species is primarily due to charge withdrawal from the central atom.[3b,25] In H_2SiXY (X ≠ Y) species, however, hyperconjugation in the X → Y and Y → X directions will be asymmetric and net bond contraction/ elongation is to be expected, as in X = F, Y = NH_2.[3c]

The O–C–O and O–Si–O angles in Table 1 are similar, both ranging from 105 to 114°, and provide evidence for hyperconjugation. We find that negative hyperconjugation in X–A–Y species (X → Y and/or Y → X) favours *increased* XAY angles.[3b,3c,26] The O–Si–O angles in the dihydroxy species are significantly greater than tetrahedral, as are the O–Si–O angles between pairs of anomerically interacting oxygen atoms in the tetrahydroxy species.

The group separation reaction (1)[2a] provides a quantitative measure of the effect of negative hyperconjugation. The calculated energies are all positive (Table 1) and increase with increasing substitution at both central atoms. The nonadditivity effect at silicon is about half as large as at carbon, though the trends are quite similar. Total separation of all four substituents (equation 2) requires 29.1 kcal/mol for A = Si and 61.1 kcal/mol (cal = 4.184 J) for A = C.

$$H_{4-n}A(OH)_n + AH_4 \rightarrow H_{5-n}A(OH)_{n-1} + H_3A–OH \quad (1)$$

$$A(OH)_4 + 3AH_4 \rightarrow 4H_3A–OH \quad (2)$$

The bond separation reaction (1) measures the substituent interaction in $H_{4-n}A(OH)_n$ relative to the reference, H_3AOH, but this also is subject to $p_\pi \rightarrow \sigma^*$ negative hyperconjugation involving A–H bonds.[19d,26] Structural evidence for such $p_\pi \rightarrow \sigma^*(A–H)$ interactions in AH_3OH molecules is provided by differences in the A–H bond lengths;[3c,26a] these are consistently longer (by 0.006 to 0.021 Å) for the A–H bonds that are parallel to adjacent oxygen $p\pi$ lone pairs (see Table 1). The trends in H–Si–O bond angles in Table 1, particularly for silanol, are also consistent with σ*(Si–H) interaction. Since the electronegativity order is Si < H < C, p_π donation from oxygen lone pairs to the σ*(AH) bonds in $AH_3–OH$ is better for A = Si than A = C. Such hyperconjugative involvement of SiH bonds tends to diminish the bond separation reaction energies at silicon and enable silicon compounds to accommodate non-anomeric conformations more easily than corresponding carbon derivatives.

The present calculations show that silicon d orbitals are not responsible for the nonadditivity effects found in these molecules. The bond separation energy for $H_2Si(OH)_2$ is in fact slightly higher at the 3-21G level which does not include any d functions (Table 1). This is in agreement with the results of Hargittai and Seip,[19a] who performed calculations on non-optimized geometries. Natural bond and localized molecular orbital analysis,[27] as applied in our studies of F–Si–F[3b] and F–Si–NH_2[3c] interactions, shows the *unimportance* of d orbital participation. For instance, second-order perturbation analysis[27] shows the π(O) → 3σ*(Si–O) interaction in $Si(OH)_4$ to be about five times stronger than the π(O) → 3d(Si) interaction (20 vs. 4 kcal/mol, respectively). By natural population analysis,[27b] the total central atom 3d occupancies in $C(OH)_4$ and $Si(OH)_4$ are 0.021 and 0.056 e, respectively. Mulliken-type population analyses of H_6Si_2O and $Si_2O_7^{-6}$ have been claimed to indicate considerable π(O) → 3d(Si) bonding,[18c,19c] but such methods divide the electron density equally between the *high-energy* silicon 3d and the *low-energy*

oxygen 2p orbitals and result in incorrect or misleading interpretations.[27b,c]

We conclude that anomeric effects operate in silicon compounds, even though silicon is rather electropositive. We have shown recently[3b,c] that the anomeric effects are even stronger at centres (such as C, P, S) which have *intermediate* electronegativities. As a consequence, silicon compounds exhibit increased conformational flexibility and reduced energies of reaction (1) relative to their carbon analogues.[3b,c]

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