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STABILIZATION OF SILICENIUM IONS BY SECOND ROW π-DONOR SUBSTITUENTS. AN AB INITIO STUDY.

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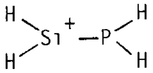
SUMMARY: PH_2 despite its strong inherent π-donor ability, stabilizes silicenium ions less than NH_2 because of the high barrier to pyramidalization at phosphorus which destabilizes the planar $H_2PSiH_2^+$. $HSSiH_2^+$ and $HOSiH_2^+$ have similar stabilities while $ClSiH_2^+$ is less stable than $FSiH_2^+$.

In contrast to carbenium ions, the analogous trivalent positively charged silicon cations (silicenium ions) have proven to be elusive chemical species. Numerous experimental attempts to observe $R_3 Si^+$ ions in solution have uniformly failed.[1] Although silicenium ions can be observed in the gas phase, their stabilities have been measured for only a limited number of substituents.[2] We have therefore undertaken a systematic theoretical study of substituted silicenium ions. In a previous paper we reported that π-donors such as NH_2 and OH are much less effective in stabilizing silicenium ions than in stabilizing carbenium ions.[3] This poor stabilization may result from the different sizes of the interacting orbitals (i.e., the 3p(Si^+) and the 2p(N) lone-pair orbitals), which reduces their overlap. Second row substituents, particularly R_2P and RS, where 3p-3p conjugation occurs may therefore be more effective in stabilizing silicenium ions. The smaller electronegativities of P (2.1 on Pauling scale) vs. N(3.0) and of S(2.5) vs. O(3.5) would, in addition, cause less inductive destabilization of Si^+ by the second row substituents (P and S).[4] In this paper we investigate this problem theoretically by studying $H_2PSiH_2^+$ (1), $HSSiH_2^+$ (2) and $ClSiH_2^+$ (3).

Calculations were performed using the Gaussian 70 series of programs[5] with full geometry optimization at both the minimal STO-3G[6a] and the split-valence 3-21G[6b] basis set levels. For $H_2PSiH_2^+$ and $HSSiH_2^+$ several conformations were considered: planar (1p,2p), perpendicular (1pr,2pr), pyramidal planar (1pp) and pyramidal perpendicular (1prp). The total and relative energies (STO-3G and 3-21G) of the cations 1-3 and of the corresponding first row substituted cations 4-6 are reported in the Table.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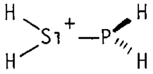
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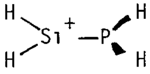
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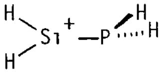
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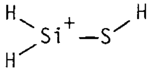
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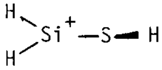
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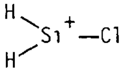
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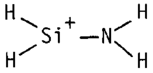
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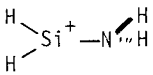
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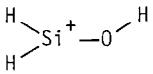
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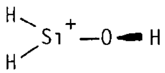
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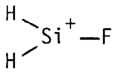
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TABLE - TOTAL ENERGIES (hartrees), RELATIVE ENERGIES (kcal mol^{-1}) and ENERGIES (kcal mol^{-1}) FOR EQUATIONS 1 AND 2

Cation	Total Energies[a]		Relative Energies		Equation 1[b,g]		Equation 2[b,g]	
	STO-3G	3-21G	STO-3G	3-21G	STO-3G	3-21G	STO-3G	3-21G
1p	-624.60514	-628.38778	16.1	2.3	4.5	6.7	-33.8[d]	-27.0[d]
1pp	-624.63087	-628.39142	0.0	0.0	20.6	9.0	-17.7[d]	-24.7[d]
1pr	-624.53199	-628.33693	62.0	34.2	-41.4	-25.2	-46.5[d]	-36.6[d]
1prp	-624.62167	-628.38101	5.8	6.5	14.8	2.5	9.7[d]	- 9.0[d]
2p	-680.32312	-684.39571	0.0	0.0	22.7	4.5	1.4[e]	-12.8[e]
2pr	-680.29579	-684.37508	17.2	12.9	5.5	-8.4	-3.0[e]	-13.4[e]
3	-741.12557	-745.54788	—	—	-13.9	-13.4	-20.2[f]	-6.5[f]
4p	-341.48471[c]	-343.61560	0.0	0.0	38.3	33.8		
4pr	-341.43186	-343.57998	33.2	22.3	5.1	11.4		
5p	-360.97548[c]	-363.31950	0.0	0.0	21.3	17.3		
5pr	-360.95523[c]	-363.29994	12.7	12.3	8.5	5.0		
6	-384.57109[c]	-387.17450	—	—	6.3	-6.9		

[a] All structures are fully optimized at STO-3G and 3-21G, respectively. [b] Energies of the neutral species will be reported elsewhere. [c] From Ref. 3. [d] X = PH_2, Y = NH_2, 1p and 1pp are compared with 4p, 1pr and 1prp with 4pr. [e] X = SH, Y = OH, 2p and 2pr are compared with 5p and 5pr, respectively. [f] X = Cl, Y = F. [g] Negative energies indicate that the equations are exothermic in the direction indicated by the arrow.

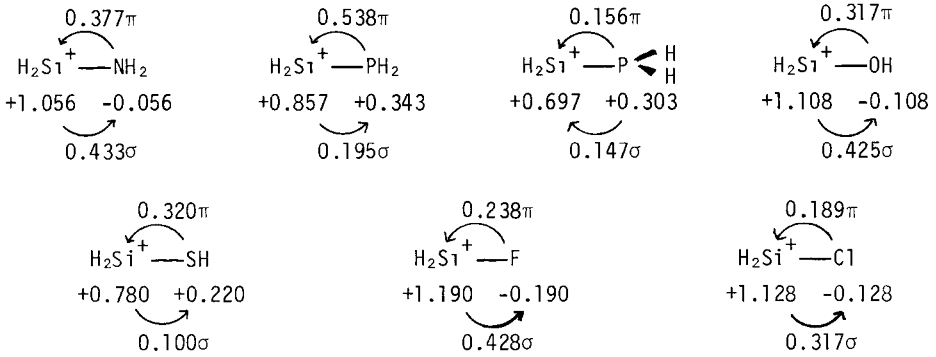
The stabilities of 1-3 are compared with that of the parent H_3Si^+ by means of the isodesmic Equation 1 and with the corresponding first row substituted cations 4-6 in Equation 2. The results are presented in the Table.

$$XSiH_2^+ \text{ (or } YSiH_2^+\text{)} + SiH_4 \rightarrow H_3Si^+ + H_3SiX \text{ (or } H_3SiY\text{)} \qquad (1)$$

$$XSiH_2^+ + SiH_3Y \rightarrow H_3SiX + H_2SiY^+ \qquad (2)$$

$$X = PH_2,\ SH,\ Cl;\ Y = H_2N,\ OH,\ F$$

According to the calculations (Table) second row π-donor substituents are less effective (SH is probably an exception, see below) than the corresponding first row substituents in stabilizing silicenium ions. PH_2 is especially disappointing; $H_2PSiH_2^+$ is less stable than $H_2NSiH_2^+$ by 17.7 kcal mol^{-1} (STO-3G), 24.7 kcal mol^{-1}(3-21G). At both STO-3G and 3-21G, H_2P is even less stabilizing than HS, while H_2N is considerably more stabilizing than OH. Mulliken population analysis[7] reveals, however, that PH_2 is a very strong π-donor, stronger even than NH_2. The Mulliken $p\pi$-$p\pi$ orbital overlaps (STO-3G) are 0.230 in planar $H_2SiPH_2^+$ (1p) compared with 0.204 in planar $H_2NSiH_2^+$ (4p).[8] π-Charge transfer from the substituent to the empty Si(3p) orbital is more extensive with PH_2 (0.538 electrons) than with NH_2 (0.377 electrons, see Scheme). Furthermore, the inductive σ-electron withdrawal is much higher for NH_2 than for PH_2 so that on the whole PH_2 is a strong electron donor (0.343 electrons) while NH_2 is a weak electron withdrawing substituent (0.056 electrons, Scheme). The strong π-conjugation in $H_2PSiH_2^+$ is exemplified in the high rotation barrier 1p → 1pr of 45.9 kcal mol^{-1}(STO-3G), compared with 33.2 kcal mol^{-1}(STO-3G) in $H_2NSiH_2^+$.



SCHEME - Gross charges of the H_2Si^+ and the X moieties in $X\text{-}SiH_2^+$, together with σ and π electron transfers (STO-3G).

If PH_2 is such a strong π-donor, why is it a poor stabilizing substituent (Eq. 1, Table). We suggest that the main reason is the high barrier to pyramidalization at phosphorus. Pyramidal PH_3 for example is more stable than planar PH_3 by 61.4 (STO-3G) and 30.7 kcal mol^{-1} (3-21G, 31.5 kcal mol^{-1} experimental[9]). Similarly, in perpendicular $H_2PSiH_2^+$ pyramidalization at P (i.e., 1pr → 1prp) stabilizes the cation by 27.7 kcal mol^{-1} (3-21G), although the phosphorus' lone pair remains in the nodal plane of the $3p(Si^+)$ orbital and π-conjugation does not occur. Planarization at P is so costly energetically that despite reduction upon pyramidalization in π-donation by the PH_2 group, the pyramidal structure 1pp is more stable than the planar structure 1p by 16.1 kcal mol^{-1} (STO-3G), 2.3 kcal mol^{-1} (3-21G). The weaker π-donation to Si^+ in 1pp relative to 1p is compensated by a reversal in the σ-electronic effect of the PH_2 group, so that the charge of the H_2Si^+ fragment in 1pp and in 1p is nearly equal (Scheme). In conclusion, PH_2 stabilizes silicenium ions poorly despite being a strong inherent π-donor,[10] because of its high barrier to inversion. However, a phosphorus substituted by an electron accepting group, e.g., C=O, C≡N, $-Si(CH_3)_3$ is known[11] to have a significantly smaller planarization energy. Such a PR_2 substituent may prove to be superior at stabilizing Si^+. We are currently examining such species computationally.

In contrast to the case of PH_2 vs. NH_2, SH and OH stabilize silicenium ions to a similar extent (STO-3G, Table).[12] Both the Mulliken pπ-pπ orbital overlaps (STO-3G, 0.150 in $HSSiH_2^+$ and 0.162 in $HOSiH_2^+$) and the π-donation to the H_2Si^+ fragment (Scheme) are similar in the two cations. Only HS, however, is a net electron donor; OH actually withdraws 0.108 electrons from the H_2Si^+ fragment. The smaller energy difference between the interacting orbitals in $HSSiH_2^+$ ($3p(S)\text{-}3p(Si^+)$) compared with $HOSiH_2^+$ ($2p(O)\text{-}3p(Si^+)$) also contributes to the stability of $HSSiH_2^+$. Both Cl and F are destabilizing relative to hydrogen at 3-21G,[13] chlorine being the more destabilizing.

We conclude that H_2P and Cl stabilize the silyl cation less than H_2N and F, respectively, while SH and OH provide similar stabilization, in contrast to the conclusions which might be drawn from qualitative PMO arguments.[4] Hopefully, this paper will prompt experimental studies in the gas phase which will enable evaluation of the reliability of the currently used basis sets for silicon and extend our understanding of these interesting substituent effects.

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10. Similar conclusions were reached recently regarding $H_2PCH_2^+$; see: Clark, T.; Schleyer, P.v.R. Tetrahedron Lett. **1979**, 4641.
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13. Here the 3-21G values are probably closer to the true values, as the STO-3G basis set is known to operate especially poorly for F.

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