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MNDO STUDY OF PHOSPHINE- AND AMINE-SUBSTITUTED SILICENIUM IONS

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Summary: MNDO calculations indicate that substituted phosphines (PR_2) and amines (NR_2) are capable of providing considerable stabilization to silicenium ions.

Ab initio calculations have been used to survey the ability of simple first (Li → F)[1,2] and second row (P → Cl)[3] substituents to stabilize trivalent silicon cations (silicenium ions). The substantial success of MNDO[4] semi-empirical calculations in describing molecules containing second row elements (Si,[5,6] P,[7-10] S,[11-13] Cl[14]) suggested their utilization in the silicenium ion problem. Application of the MNDO methodology to silicenium ions substituted by simple first and second row hydrides showed[15] a good qualitative agreement with non-empirical theory with regard to both energies and geometries. Based on this observation, and the clear advantage of greatly reduced computation expense enjoyed by MNDO, its further application as a guide to solution studies of substituted silicenium ions seemed most desirable. In particular, as the concept of substitution on a silicon of groups that stabilize a carbon cation has uniformly failed[16] to produce a solution stable silicenium ion, the computational screening of new, non-carbon-inspired substituents by MNDO was further warranted.

In this regard our a priori rationale was that a phosphine would be an excellent group for stabilizing a silicenium ion. This was based on the expected superior 3p-3p π-conjugation of a $P\text{-}Si^+$ moiety vs. the 2p-3p π-conjugation in a $N\text{-}Si^+$, as well as the smaller inductive destabilization of P (2.1 on the Pauling scale) vs. N (3.0). The computational results[3,15] for $PH_2\text{-}SiH_2^+$ were, however, disappointing. Despite being a stronger π-donor and a weaker σ-withdrawing group relative to NH_2 in $NH_2\text{-}SiH_2^+$ (as evidenced by Mulliken population analysis)[3] all methods of calculation predicted PH_2 to be decidely inferior to NH_2 at stabilizing Si^+, i.e., NH_2 is more stabilizing than PH_2 by 25.2 kcal/mole, MNDO (Table 1); 24.8 kcal/mole[3], 3-21G; 17.7 kcal/mole[3], STO-3G as defined by the isodesmic Equation 1.

$$XSiH_2^+ + SiH_4 \rightarrow XSiH_3 + SiH_3^+ \qquad (1)$$

Table 1 - Total Energies (eV) and Energies for Equation 1 (kcal/mole)

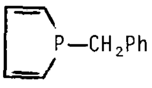
X	$XSiH_3$	$XSiH_2^+$	Energy Eqn. 1[a]
PH_2	-321.94941	-298.49683	2.5
NH_2	-373.94051	-351.58113	27.7
PC_4H_4[b]	-861.41711	-838.40427	12.6
NC_4H_4[c]	-912.70232	-889.89612	17.4
$P(CHO)_2$	-1222.78008	-1199.58497	8.5
$P(SiH_3)_2$	-569.66496	-547.25263	26.1
$N(SiH_3)_2$	-662.03957	-599.82872	31.1
$P(OH)_2$	-968.90607	-946.42167	24.8

[a] Postive values for energy mean that the equation is endothermic in the direction indicated by the arrow. [b] PC_4H_4 = phosphole. [c] NC_4H_4 = pyrrole.

We suggested that the inability of PH_2 to meet our expectations was due in large part to the high barrier to planarization at phosphorus[3] ($E_{inversion} PH_3$,31.5 kcal/mole).[17] The planarization at P required for effective π-donation is so costly energetically in $PH_2SiH_2^+$ that little net stabilization can be provided to the cation. In fact, both ab initio (STO-3G,[18] 3-21G[19]) basis sets predict a pyramidal P in this cation.[3]

Based on our earlier results,[15] MNDO appeared to be an excellent means of assaying the validity of this suggestion. Because of the implied involvement of $E_{inversion}$ at P and its ability to stabilize Si^+, the excellent agreement of the MNDO calculated planarization energy of PH_3 (31.5 kcal/mole experiment,[17] 30.0 kcal/mole MNDO) with experiment added further credibility to the use of this methodology.

The key investigation centered on the ability of PR_2 derivatives with substantially lower planarization energies than PH_3 to stabilize Si^+. Experimental evidence suggests that the use of sterically bulky R groups to lower the barrier to inversion is ineffective, e.g., PH_3 and dialkylphenyl phosphines have essentially equal planarization energies.[20] Three electronic effects, however, have been proven to have a considerable effect on $E_{inversion}$ at P: 1) incorporation of the phosphorus lone pair into an aromatic $4n + 2\pi$ system; 2) substitution by groups capable of p-p(π) conjugation; 3) substitution by groups of low electronegativity.[20] For example, the $E_{inversion}$ of the P in phosphole 1 decreased to an experimental value of 15 kcal/mole.[20,21] The effects of conjugation and electronegativity are demonstrated by the $E_{inversion}$ of P in compounds 2 and 3 which have experimental values of 19 kcal/mole.[21,22]



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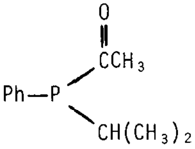

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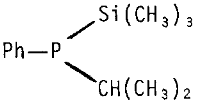

3

Evaluation by MNDO of the incorporation of aromaticity, p-p(π) conjugation, and electropositive groups on the ability of PR_2 to stabilize a silicenium ion is summarized in Table 1. The effects of identically substituted NR_2-SiH_2^+ are also given for comparison.

Inclusion of the phosphorus lone pair into a phosphole ring has a sizeable effect on the degree of stabilization provided to PH_2 (2.5 → 12 kcal/mole). The NR_2 group, with an inherent low $E_{inversion}$, suffers on incorporation into an aromatic pyrrole ring due to a lessening of its π-donating ability. As a result, pyrrole is less efficient at stabilizing Si^+ relative to NH_2 by 10.3 kcal/mole. Substitution of π-conjugating group on P such as a carbonyl realizes a more modest improvement relative to PH_2 (2.5 → 8.5 kcal/mole). Although not calculated, an amide would undoubtedly be less stabilizing than NH_2. The fact that the π-electron poor (relative to PH_2) diacyl phosphine and phosphole are more effective than PH_2 at stabilizing Si^+ is strong support for the overall importance of the inversion barrier at phosphorus to silicenium ion stabilization.

The largest effect is seen upon substitution of a SiH_3 (low electronegativity and possible $d\pi$-$p\pi$ conjugation[23]) on phosphorus which results in a dramatic 24 kcal/mole of added stabilization relative to PH_2. $P(SiH_3)_2$ enjoys not only a low barrier to planarization but also a relatively unencumbered π-system, the result of which is a superior Si^+ stabilizing moiety. $N(SiH_3)_2$ also benefits relative to NH_2 presumably due to its lower inductive withdrawal and the lower barrier to inversion at N.[24] The effect of NR_2 is, however, much smaller allowing the NR_2 and PR_2 groups to have comparable stabilizing ability (31.1, 26.6 kcal/mole, respectively).

$P(OH)_2$ was next examined because it provided an interesting conflict of opposing effects inverse to those operating in the phosphole or diacyl phosphine. On one extreme, it is predicted[20] to have a very high barrier to planarization and should be incapable of achieving this optimal geometry for π-stabilization. Alternatively, it possesses an electron-rich π-system which should be effective at delocalization into the empty p orbital on silicon.

The calculations reveal that $P(OH)_2$ is very effective at stabilizing Si^+ (24.8 kcal/mole). Interestingly, the optimal geometry for this cation, however, shows a pyramidal phosphorus which has rotated an electron-rich P-O bond into coplanarity with the empty p orbital on Si,[25] in effect, opting for a different mode of stabilization, i.e., hyperconjugation.

Multiple Substitution - The effect of multiple substitution of PR_2 and NR_2 groups was evaluated by means of isodesmic equations 2 and 3. The results are given in Table 2. The calculations indicate a leveling effect in the stabilizing ability of NH_2 presumably due to the debilitating

$$X_2SiH^+ + SiH_4 \rightarrow H_3Si^+ + H_2SiX_2 \qquad (2)$$

$$X_3Si^+ + SiH_4 \rightarrow H_3Si^+ + HSiX_3 \qquad (3)$$

σ-withdrawing nature of this group. Alternatively, PH_2 does not suffer such an effect. The leveling is less pronounced for $N(SiH_3)_2$ due to its smaller inductive-withdrawing capacity. The tris (disilylamino)- and tris (disilylphosphino)-silicenium ions are the most stable silicenium ions yet evaluated.

Table 2 - Total Energies (ev) and Energies of Equations 1, 2 and 3 (kcal/mole)

	Total Energy				Energy of Equations		
X	X SiH	X_2SiH^+	X_3SiH	X_3Si^+	1	2	3
H_2N	-596.51212	-574.66349	-819.07832	-797.33202	27.7	39.5	41.9
H_2P	-492.52430	-469.39002	-662.94735	-640.12863	2.5	9.8	17.1
$N(SiH_3)_2$	-1092.67629	-1070.98520	-1563.29250	-1541.93767	31.1	43.1	50.9
$P(SiH_3)_2$	-987.99788	-966.00724	-1406.32474	-1384.75446	26.1	36.2	45.9

Geometries of the Cations - The amino cations all adopt totally planar structures with the exception of the bis- and tris-disilyl amine compounds which must twist around the N-Si bond out of the all-planar configurations to avoid severe steric interactions. The N, however, remains planar. The geometries in the phosphino cations can be rationalized based on the interplay of the following factors: 1) the inherent tendency towards a pyramidal form of a given PR_2; 2) the relative ability of the lone pair on phosphorus to delocalize into the empty p orbital on Si vs. into another π-conjugating group (e.g., C=O) as a function of pyramidalization at P; 3) hyperconjugating ability of PR_2; 4) steric effects. As a result, H_2Si^+-PH_2 is totally planar, although the energy difference between this form and one with a pyramidal PH_2 is small. On substitution of two and three PH_2 groups on Si^+ the phosphorus reverts to being pyramidal, apparently due to steric effects. The lone pairs on PR_2 and the empty p orbital are, however, essentially coplanar. The mono-disilylphosphino cation is planar. The bis-disilylphosphino cation has one PR_2 in the plane of the silyl cation and one twisted 90° presumably due to factors 3 and 4. The trisdisilylphosphine has each PR_2 moiety twisted moderately out of the plane of the silicon cation due to a balancing of steric and electronic effects. The phosphines are planar throughout this series. The phosphole-substituted silicenium ion is pyramidal at phosphorus with the lone pair on P coplanar with the empty orbital on Si. Perhaps pyramidalization affects the 3p-3pπ interaction less than the delocalization with the 2pπ system (factor 2); i.e., the lone pair avoids "losing" density to the aromatic system while still providing it to the cation.

Conclusion - Control of the planarization energy of phosphorus and the inductive-withdrawing nature of nitrogen has allowed these substituents to become highly effective at stabilizing silicenium ions. Application of these results to experimental work is in progress.

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25. The alternative geometry of a pyramidal P with the lone pair coplanar with the empty P orbital on Si is <1 kcal/mole less stable.

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