Synthesis and Characterization of Bisilylated Onium Ions of Group 15 Elements
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An Example: NMR Characterization of the Phosphonium Ion
A symmetric cation is formed upon ionization of the phosphino-substituted disilane as it is shown by its NMR spectra. The down-field shift of the single $^{29}$Si resonance in the cation indicates some uptake of positive charge and the decrease of the $J_{Si}$ coupling constant is in qualitative agreement with a weaker SIP bond in the cation. Quaternization of the phosphor in the cation, interestingly, has only small influence on the $^{31}$P NMR chemical shift. Quantum mechanical calculations of structure and NMR chemical shifts for a close model are in good agreement with the experimental data. This confirms the validity of the calculated structure.

Calculated structure and NMR parameters

Bonding Situation in Bisilylated Onium Ions
Intramolecular Stabilization Energy $E^{***}$

$E^{***}$, the energy difference between the open silyl onium and the cyclic onium ion, is maximal for $E=P$ and it markedly decreases from $P$ to $Bi$.

The calculated atomic charge at silicon is largest for the amino substituent and it decreases by ca. 0.5 a.u. for the phosphonium ion, while it remains nearly constant for the arsonium and stibonium ion.

Calculated atomic and group charges (in a.u., NBO)

Charge transfer from the $EMe_{2}$ unit to the Me$_2$Si-$R$ group as predicted by an NBO analysis is very small for the amino group but it is considerably larger for the phosphino group. It remains approximately constant for the arsonium and stibonium cations.

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The tetravalent onium ions of the elements N-$>$Sb could be synthesized in clean reactions between the precursor silanes and triyl cation. The cations are identified by multinuclear NMR spectroscopy and were structurally characterized by quantum mechanical calculations for close models of the cations in the gas phase.

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