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INTRAMOLECULAR INTERACTION IN THE CHEMICAL BEHAVIOR OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS

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2.1 INTRODUCTION

In many respects the unusual behavior of carbon-functional organosilicon compounds, i.e., compounds in which silicon is bonded to an sp³ hybridized carbon of an organic framework containing a functional group,

\[ \text{Si} \cdots (C)_n \cdots \text{functional group} \]

[functional group = a group bonded to the \((C)_n\) framework by an atom other than a formally neutral sp³ carbon] is associated with a greater atomic volume, a lower electronegativity, and more polarizable bonds of silicon compared to carbon (Chapter 4, Section 4.4). The greater atomic volume of silicon makes steric shielding less significant; in silacyclic compounds the greater atomic volume adds conformational effects that change torsional angles and transannular repulsions between non-bonded substituents of the ring. The lower electronegativity of silicon in trialkylsilyl substituted compounds creates a negative charge on the adjacent carbon, and the inductive mechanism provides the following charge distribution in a silyl-alkyl framework

\[ \delta^- \delta \delta^- \delta \delta^- \]

\[ R_3\text{Si} \cdots +C \cdots +C \cdots +C \]

The opposite charge distribution is to be expected in this system when alkyl groups on silicon are replaced by more electronegative substituents.

V. Chvalovský et al. (eds.), Carbon-Functional Organosilicon Compounds
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This inductive mode of electron displacement is often accompanied by other types of intramolecular interactions. Thus, in \( R_3Si-C-C\delta^\pm \) systems a hyperconjugative mode of electron displacement becomes important (Chapter 4, section 3). The silicon atom appears able to stabilize reaction intermediates either by donating electrons to an electron deficient \( \beta \)-carbon, or by withdrawing electrons from this atom when it is electron rich.

The importance of this conjugative mechanism increases with the electronic demands of the reaction center.

Another mode of intramolecular interaction occurring in carbon-functional organosilicon compounds (carbon-functional silanes) is through-space interaction between silicon and a functional group (Chapter 4, section 4.5) or between silicon and a reaction center created in, e.g., an intermediate species. Intramolecular interactions take place in compounds in which the functional group can approach the silicon easily \((n > 2)\), and in compounds \((n = 1)\) where such an interaction is impeded by some distortion of the \( \text{SiC} \) (functional group) bond angle.