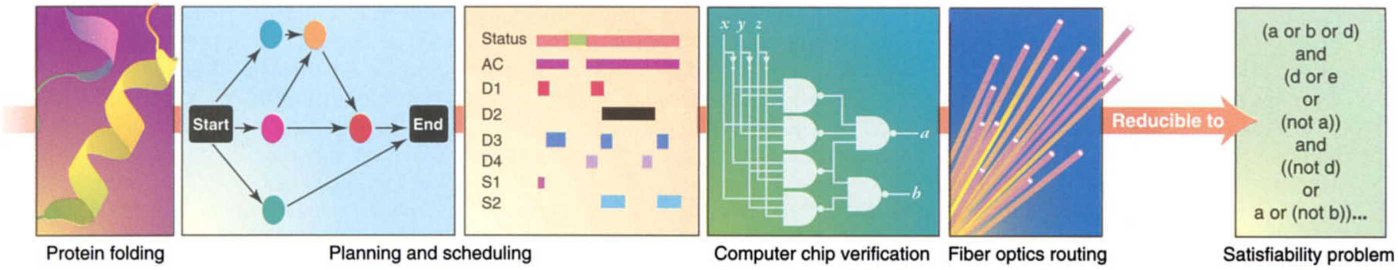

A variety of problems reducible to the satisfiability problem.

An approach that is often effective for solving the K-SAT problem is called local search. The search starts from a randomly generated truth assignment. One then changes or "flips" the truth value of one of the variables to try to satisfy more of the constraints. Such flips are repeated until a satisfying assignment is found. However, the set of possible truth assignments is exponentially large—2^N truth assignments for N variables. A large number of flips may be required, depending on the structure of the search space (*9*).

Mézard *et al.* (*1*) provide a remarkably detailed picture of the search space of a random K-SAT problem and introduce a new algorithm for finding a satisfying assignment. The algorithm is based on the cavity method from statistical physics. In this approach, the concept of a cavity field is used to measure the tendency of a variable to be "True" when one of the clauses containing the variable is removed from the SAT problem. In effect, the method exploits the topology of the search space to navigate efficiently through the exponentially large set of assignments.

The authors show how the search space for $k \geq 3$ changes dramatically when one approaches the phase transition region. For $k = 3$ and $\alpha < 3.92$, the search space is globally smooth, with the solutions grouped together. A basic local search method can find a satisfying assignment relatively quickly. However, for larger values of α, the space breaks up into a number of metastable states, signaling the onset of search complexity. A basic local search method will get "stuck" at assignments with a nonzero number of unsatisfied clauses. In such cases, Mézard *et al.*'s method still has a high probability of finding a satisfying assignment.

Mézard *et al.*'s technique is general and holds promise for a wide range of hard computational problems. However, because SAT problems in real-world applications are not random, the approach may have to be adapted for SAT problems that are more structured (*10–13*). The work illustrates the power of bringing together ideas and techniques from statistical physicists interested in disordered systems, mathematicians studying combinatorial structures, and computer scientists studying computational complexity.

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PERSPECTIVES: SILICON CHEMISTRY

R_3Si^+—Free at Last

Peter P. Gaspar

Cations containing a tri-coordinate silicon atom, R_3Si^+, well separated from counterions and solvent molecules have been avidly sought for decades (*1*). On page 825 of this issue, Kim *et al.* (*2*) bring this search to a successful conclusion by presenting the crystal structure of the salt of such a cation.

Silicon is in the same group as carbon and shares some of its chemical characteristics. But silicon chemistry often follows pathways different from those of carbon. To understand reaction mechanisms for silicon compounds, one must synthesize and study silicon analogs of the reactive intermediates of organic chemistry.

The trivalent silyl cation R_3Si^+ has been particularly challenging. To solve this problem, chemists have had to view the covalent bond in shades of gray rather than black and white—as a continuum of electronic interactions of varying strength, rather than as a link between atoms that is either present or absent. New quantitative probes for the extent of bonding of ions with surrounding species had to be developed, and a seeming paradox had to be resolved: Why are R_3Si^+ cations difficult to detect in solution, yet comparatively easy to make in the gas phase (*3*)?

In normal organosilicon compounds, $R_3Si\text{-}Z$, silicon is attached to four groups. How can an Si-Z bond be broken in such a manner that a trivalent silicon cation is created? Researchers have looked to analogous carbon compounds, $R_3C\text{-}Z$, for answers. But most Z groups that easily ionize from $R_3C\text{-}Z$ to form R_3C^+ do not readily depart from the silicon compound because the Si-Z bonds are stronger than the equivalent C-Z bonds.

Hydrogen is unusual in that C-H bonds are stronger than Si-H bonds. Hence transfer of a hydride ion, H^-, from R_3SiH to a carbon cation could lead to the formation of a silyl cation. But when the salt of a carbon cation was used as a hydride acceptor (*4*), the products proved to be silyl esters (*5*). If a silyl cation formed at all, it was immediately consumed by the counterion.

Why can a carbon cation, Ph_3C^+, persist in the presence of ClO_4^-, but a silyl cation, R_3Si^+, is immediately captured by this anion? Silicon forms a much stronger bond with oxygen than does carbon, and silicon cations are stabilized to a lesser ex-

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The author is in the Department of Chemistry, Washington University, St Louis, MO 63130, USA. E-mail: gaspar@wuchem.wustl.edu

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tent than their carbon analogs by distributing their positive charge over attached groups. This lessened charge "delocalization" can be understood by comparing trivalent silicon and carbon cations (see the figure).

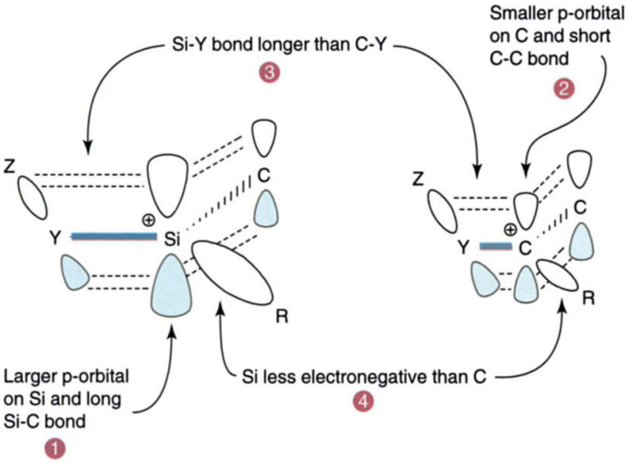
Attempts to stabilize silyl cations through the ionization of silyl perchlorates, $R_3Si\text{-}OClO_3$, encountered new problems (*6*). Salts were formed, but the cations, initially thought to be free R_3Si^+ (*7*), were revealed by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy (*8*) to be complexes of the desired silyl cations with solvent molecules ("Solv") involving some degree of covalent bonding. The silicon atoms in these complexes, which we can represent as $R_3Si\cdots\cdots Solv^+$, are between three- and four-coordinate, and most of the positive charge is carried by the solvent molecule.

Progress toward free R_3Si^+ came with the development of counterions and solvents less prone to forming bonds with a silyl cation. A major breakthrough was the discovery that simple aromatics like benzene or toluene were sufficiently polar to dissolve silyl cations and suitably noncoordinating counterions (*9*).

With simple alkyl substituents on silicon, salts of R_3Si^+ with perfluorotetraphenylborate counterions, $(C_6F_5)_4B^-$, were formed. NMR spectra indicated, however, that the silyl cations were still not entirely free (*9*). Loose coordination with solvent was confirmed by an x-ray structure of Et_3Si^+ $(C_6F_5)_4B^-$ crystallized from toluene (*10*). The crystal structure was interpreted as a silyl cation with no coordination to its counterion but distant coordination to a solvent molecule. The nature and extent of this coordination were controversial. Linus Pauling, in one of the last papers published in his lifetime, deduced a bond order of 0.35 for the $Et_3Si^+\cdots\cdots$toluene complex, meaning that 65% ionic character was assigned to this silyl cation in a solid-state environment (*11*).

For a free R_3Si^+ cation, the bonds to the three pendant groups should lie in a plane, and the average bond angle to the tricoordinate silicon should be 120°. In the solid-state $Et_3Si^+\cdots\cdots$toluene complex, the average angle was only 114° (*10*). With a different counterion, Reed *et al.* achieved a bond angle of 117° in an intimate ion pair with iPr_3Si^+, and deduced a Pauling bond order of 0.40 (*12*, *13*).

From the quantitative criteria available in the mid-1990s, Reed and Lambert concluded that the freest silyl cations observed in the condensed phase until then were only about one-third to two-thirds of the way from a tetracoordinate silane to a tricoordinate silyl cation (*6*, *12*). Calculations suggested that some complexation of R_3Si^+ occurs even in species with cation affinities as low as those of methane, argon, and neon (*14*). These calculations seemed to indicate that R_3Si^+ could never be free of complexation in any solvent, leading Arshadi *et al.* to conclude that "the free silylium cation in solution is a fiction" (*15*).



Comparing like with unlike. The vacant p orbital holding most of the positive charge on R_3Si^+ is larger (**1**) than the corresponding orbital on R_3C^+ (**2**), and the Si-C bond is longer than the C-C bond. Si-C π-bonding is therefore weaker than C-C π-bonding (**1**, **2**). Donation of σ-electron density to Si from adjacent Y-Z bonds is diminished relative to C by the longer Si-Y bond (**3**). The Si atom of R_3Si^+ is less able to attract the electron pair that it shares with an attached R group than is the C atom of R_3C^+ because of the lower electronegativity of Si (**4**).

But Lambert and Reed were not deterred. They searched for bulky substituents R that could keep both solvent molecules and counterions at a distance from the tricoordinate silicon atom beyond the range of complexation. The mesityl group, 2,4,6-trimethylphenyl (Mes), led to success, but only after another problem was overcome. The bulk of the Mes groups prevented the generation of Mes_3Si^+ from Mes_3SiH by removal of a hydride ion, because the reagent that accepted hydride from less crowded R_3SiH molecules could not come close enough to abstract the H^- from Mes_3SiH (*9*).

Lambert and Zhao cleverly replaced the hydride leaving group by attaching to Mes_3Si a long narrow group, $CH_2CH{=}CH_2$, which extended beyond the congested space dominated by the mesityl groups and could thus be attacked by an electrophile (*16*). ^{29}Si NMR showed that the product of this reaction was a Mes_3Si^+ silylium ion free of interaction with its counterion Y^- and with solvent molecules: The observed chemical shift matched that predicted by calculations for the gas-phase ion and stayed constant with changes in the counterion and solvent. The one further piece of desired evidence—the detailed geometry from an x-ray crystal structure—is provided in this issue (*2*).

Is there room for further argument? Of course, there always is. The Mes_3Si^+ cations are indeed far removed from their counterions and from the benzene solvent molecules (*2*). But the question will inevitably be raised whether the methyl groups that protect the cationic silicon center from external attack themselves complex the silicon center. Such intramolecular complexes of C-H bonds with transition metal are known as "agostic interactions." Reed and Lambert argue that such internal solvation is not present here. A theoretical calculation whose predictions were in close agreement with the experimental data found no sign of internal solvation.

With the latest work of Kim *et al.* (*2*), the era of silyl cation discovery is drawing to a close. But one can anticipate an equally eventful period of exploration and application.

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