

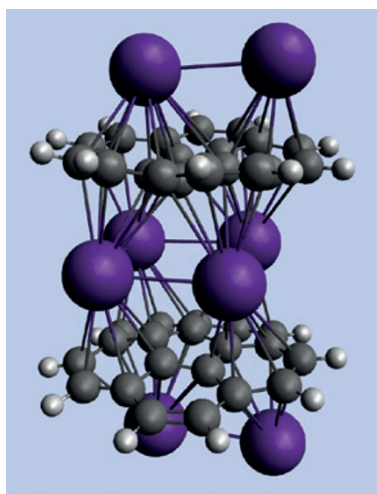
SOLID-STATE CHEMISTRY

Corannulene complexation

J. Am. Chem. Soc. **135**, 12857–12860 (2013)

Corannulene ($C_{20}H_{10}$) is a large, bowl-shaped polycyclic aromatic molecule that can be considered as a fullerene fragment. It has attracted attention for a variety of reasons, including its five-fold symmetry, and its packing and coordination behaviours, as well as its potential to exhibit superconductivity with high transition temperatures.

Superconductivity is not common in organic species, but has been observed in a number of charge-transfer complexes and doped carbon materials — and has been predicted for alkali-doped corannulene. Now, a team led by Kim Baldrige and Karl-Heinz Ernst from the University of Zurich have prepared films comprising corannulene and caesium, proposing that they have a $Cs_4C_{20}H_{10}$ composition with a dimeric structure in which four caesium atoms are sandwiched between two corannulenes. $Li_4C_{20}H_{10}$ compounds with a similar sandwich structure have previously been observed in



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solution, but it was thought that analogues with ions larger than lithium would not form.

Baldrige and Ernst co-deposited corannulene and caesium at 100 K on a copper surface in an ultra-high-vacuum chamber. Analysis by ultraviolet photoelectron spectroscopy revealed layer-

by-layer growth, in which a metallic caesium film formed that was then progressively covered by corannulene molecules. At low corannulene coverage, charge transfer from the caesium to the corannulene was observed. This is in agreement with corannulene's good electron-accepting properties — it can accept four electrons into its doubly degenerate lowest unoccupied molecular orbital. At higher coverage, an undoped corannulene multilayer formed on the caesium film. On heating in the 200–300 K temperature range, however, the caesium ions increasingly diffused into the corannulene multilayer. Above 300 K both species desorbed.

Analysis of the film by X-ray photoelectron spectroscopy obtained after annealing supported a composition with a caesium/corannulene ratio of 4:1. Theoretical calculations showed that the most stable structure is a dimer adopting a stacked conformation, with four caesium cations in a square geometry located between two distorted tetraanionic corannulenes, and two additional caesium atoms both above and below the sandwich structure. *AP*

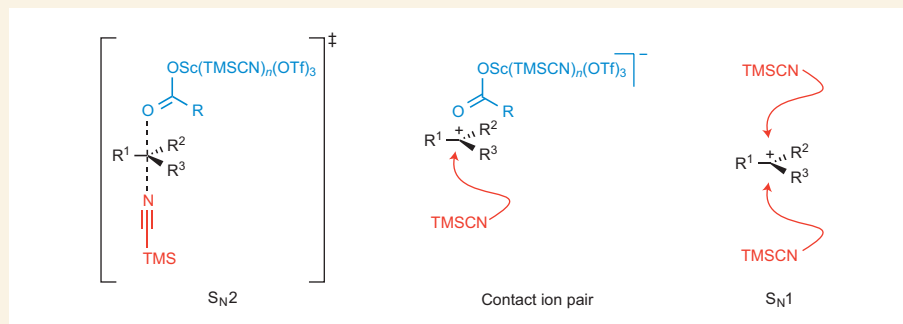
STERESELECTIVE SYNTHESIS

Inverted isocyanides

Nature **501**, 195–199 (2013)

One of the earliest pieces of mechanistic organic chemistry taught to undergraduates the world over is that S_N2 reactions proceed with an inversion of the reacting centre. This principle is swiftly followed by the fact that substitutions at a tertiary centre do not occur through an S_N2 mechanism and the alternative S_N1 mechanism results in the formation of stereochemical mixtures. Such canonical reactivity is problematic when targeting the syntheses of a number of medicinally interesting marine natural products containing tertiary isocyanides. Now, Ryan Shenvi and co-workers from the Scripps Research Institute have developed a Lewis acid-catalysed solvolysis of trifluoroacetate esters (formed from tertiary alcohols) that proceeds with an inversion of the reacting centre.

Textbook descriptions aside, substitution reactions most likely occur by mechanisms along a continuum of pathways in which the S_N1 and S_N2 are the extremes (pictured). Shenvi and co-workers were convinced that they would be able to perform their desired stereoinversion by using a Lewis acid to activate the starting material towards formation of a



carbocation (as in the S_N1 mechanism) but then quickly trap the nascent carbocation before the leaving group had fully departed. This would ensure that the nucleophile could approach from only one face (as in the S_N2 mechanism). To achieve this they planned to use a large excess of nucleophile while screening for a Lewis acid and activated ester combination that — even in the presence of this large excess of competing Lewis base — would favour activation of the ester starting material. The combination of trimethylsilyl cyanide as nucleophile with scandium triflate as Lewis acid acting on a trifluoroacetate ester was found to be just right.

The methodology is shown to be synthetically useful when starting with a variety of tertiary alcohols being converted to isocyanides — with onward conversion to amines also possible. Chemoselectivity for the reaction of tertiary over secondary and primary esters is observed with more sterically hindered centres reacting fastest — an inversion of the pattern seen for the S_N2 reaction. The products, meanwhile, are the same as those that would be expected from a putative S_N2 reaction. The high, but imperfect, inversion selectivity militates in favour of a reaction that proceeds through the rapid reaction of a contact ion-pair. *SD*