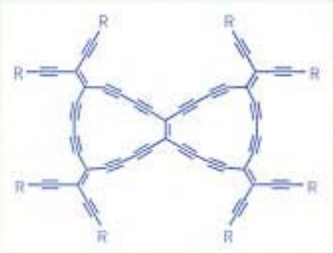
CONCENTRATES

Novel acetylenic chromophores

Molecules in a new class of conjugated all-carbon macro-cycles have been shown to be powerful electron acceptors. Organic chemistry professor François Diederich at the Swiss Federal Institute of Technology, Zurich, and coworkers prepared the compounds, which they dub "radiaannulenes," from tetraethynylethene building blocks using a scaffolding technique known as intramolecular oxidative acetylenic coupling [*Chem. Commun.*, 2003, 1634]. They used X-ray crystallography to reveal the cyclic framework of the macrocycles and cyclic voltammetry to demonstrate the compounds' strong electron-accepting power. Electronic absorption spectra reveal that the compounds display intense intramolecular charge-transfer when the mono- and bicyclic (shown) macrocycles are functionalized at the periphery by electron-donating N,N-dialkylanilino groups (R). "We are optimistic that the facile preparation protocol using versatile acetylenic scaffolding and the remarkable stability of the new materials will enable us to double or triple the core size of the radiaannulenes and also bring them to applications in devices relying on nonlinear optical or two-photon absorption properties," Diederich says.



DNA mimics target double-stranded DNA

In the past, methods using pseudocomplementary oligonucleotides—a type of DNA mimic—to target sequences on double-stranded DNA only could work at the end of a DNA duplex or required assistance from proteins. Now, Vadim V. Demidov and Irina V. Smolina of the Center for Advanced Biotechnology at Boston University report that pseudocomplementary peptide nucleic acids (pcPNAs) together with pseudocomplementary DNA oligomers (pcODNs) can target DNA sequences anywhere in the double helix without protein assistance [*Chem. Biol.*, 10, 591 (2003)]. The pseudocomplementary nucleobase analogs are designed so they won't form base pairs with each other, but they can still form Watson-Crick pairs with natural DNA bases. The pcPNA inserts into the double-stranded DNA and creates duplex edges where the pcODN can work its way into the DNA helix. Using this approach, the researchers demonstrate that they can selectively tag DNA using biotinylated pcODNs. They also show that pcODN can serve as a primer for DNA polymerase in primer-extension reactions. The authors expect this method could be useful for nondenaturing DNA sequencing, labeling, and isolation.

Acetamides offer direct CF_3 delivery

Trifluoromethyl groups im-part high lipophilicity to organic compounds, a trait particularly useful for pharmaceuticals, so chemists are continually seeking new and improved trifluoromethylating reagents. The current favorite is the commercially available $CF_3Si(CH_3)_3$, which functions as a precursor for the CF_3^- nucleophile. However, it is prepared from CF_3Br, which is an environmental concern. And CF_3^- can decompose to fluoride anion and difluorocarbene, which may limit reaction efficiency. Now, Thierry Billard and Bernard R. Langlois of Université Claude Bernard Lyon 1 in France and coworkers there and at Rhodia have devised a class of O-silylated trifluoroacetamides in which the trimethylsilyl group is separated from the trifluoromethyl group to allow direct transfer of CF_3 to a carbonyl carbon [*Angew. Chem. Int. Ed.*, 42, 3133 (2003)]. The reactivity of the trifluoroacetamides, $(H_3C)_3SiOCHRCHRNRC(O)CF_3$, was demonstrated by converting benzophenones, acetophenones, and benzaldehydes to trifluoromethylated alcohols in good yields, even at room temperature. The researchers believe the acetamides can compete with $CF_3Si(CH_3)_3$ as a commercial trifluoromethylating reagent.

Looking in on RNA folding

As RNA attracts increased attention for its various biological roles, scientists want a clear picture of how RNAs fold into their native shapes. In one approach, a team led by chemists Xiaowei Zhuang of Harvard University and Nils G. Walter of the University of Michigan use a combination of single-molecule fluorescence spectroscopy, site-specific mutations, and metal-ion titration to study transition states in the folding of a hairpin ribozyme [*Proc. Natl. Acad. Sci. USA*, published online July 17, http://www.pnas.org/cgi/doi/10.1073/pnas.1133280100]. They find that tertiary contacts involving backbone functional groups are only partially formed in the transition state, while those involving interdomain base pairs are not formed at all, even though the two helical domains are close to one another. The ribozyme folding is stabilized by both divalent and monovalent ions, suggesting that specific metal binding is not necessary for folding but that nonspecific electrostatic interactions are crucial to the process. The researchers believe that compact transition states without well-formed tertiary contacts may be a general property of elementary RNA folding reactions.

DNA-cleaving agents may aid studies on protein radicals

A new class of amino acid-based DNA-cleaving agents developed by chemists at Boston College may prove useful in studying the damaging effects of protein radicals generated in cells. Assistant professor Shana O. Kelley, graduate students Kerry P. Mahon Jr. and Erin G. Prestwich, and undergraduate Rodrigo F. Ortiz-Meoz attach a dipeptide containing tryptophan and lysine to thiazole orange, a planar molecule that binds DNA by slipping between base pairs [*Chem. Commun.*, 2003, 1956]. When exposed to visible light, the peptide-intercalator conjugate forms a tryptophan-based peroxyl radical that cleaves DNA. Photoexcitation of the intercalator generates singlet oxygen ($^1O_2$) in close proximity to tryptophan, leading to formation of the radical. Conjugates containing tyrosine instead of tryptophan behave similarly. Kelley's team hopes to use the peptide-intercalator conjugates as model systems to study the reactivity of amino acid peroxyl radicals and the dangers such species may pose to cells and their DNA.