

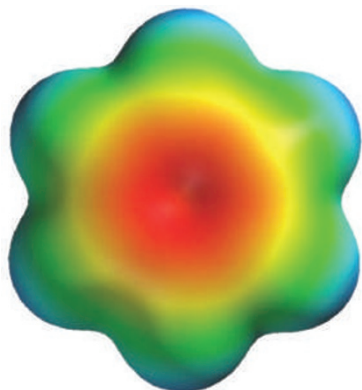
intermediates are either unstable or unreactive. Having devised a synthetic plan that circumvents these issues, and proceeded to make what they believed to be the natural product, Carreira and colleagues were presented with a new problem. Again, the polychlorinated structure was shown to be the cause.

The key step in the synthesis is an epoxide ring-opening that, under normal circumstances, could provide only the desired stereochemistry. The researchers suggested that the reaction might proceed via an unusual cyclic (chloronium ion) intermediate that reverses the stereoselectivity. This hypothesis is supported by the fact that starting with an epoxide of opposite stereochemistry gave access to the desired natural product.

SUPRAMOLECULAR CHEMISTRY

Another piece of the π

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Aromatic π - π interactions are important to many biological functions, including stabilizing the structure of DNA and the binding of ligands to enzyme active sites. Although much of the previous work to understand the nature of such interactions has been directed towards benzene and substituted-benzene dimers, efforts are refocusing on identifying the effects of heteroatoms.

Now Edward Hohenstein and David Sherrill at the Georgia Institute of Technology have studied the interactions between the individual molecules that make up pyridine–pyridine and pyridine–benzene dimers. They compared them with those of benzene–benzene dimers to understand how the presence of a nitrogen atom in the aromatic ring influences the π - π interactions. The dimers can take three different geometrical arrangements: sandwich, T-shaped and parallel displaced (a horizontally offset sandwich arrangement).

Using high-level quantum chemical calculations, Hohenstein and Sherrill investigated the bonding interactions in the various structural configurations possible in these arrangements.

The researchers saw that the inclusion of a nitrogen atom into the aromatic ring unsurprisingly creates a dipole, which is significant in pyridine–pyridine dimers but relatively insignificant in pyridine–benzene dimers. The heteroatom also diminishes the ‘reach’ of the π -electron cloud, thus reducing ‘exchange-repulsion’, and reduces the polarizability of the monomer, which lessens the effect of dispersion and induction forces.

SENSORY ARRAYS

A nose for proteins

Angew. Chem. Int. Ed. **48**, 1771–1774 (2009)

Stimulated by how the mammalian nose works, scientists have recently begun to develop sensors based on arrays of supramolecular receptors that generate a measurable signature output to identify molecules. Measuring proteins in such a way could provide an accurate method for diagnosing diseases that are characterized by protein imbalance.

Now David Margulies and Andrew Hamilton from Yale University have developed a recognition system based on DNA that can identify proteins in samples as small as a single microlitre drop. The sensors are based on G-quadruplexes — structures made up of four strands of guanine-rich DNA that self-assemble into a square arrangement. Each of the four strands can be functionalized with a fluorophore. If two different fluorophores are used, then the four strands can assemble into six different possible structures, creating an ensemble of different G-quadruplexes, each with a distinct fluorescence emission.

Non-specific interactions between a protein and the various G-quadruplex structures of an ensemble result in measurable changes to its fluorescence signature. Using an ensemble of G-quadruplexes functionalized with three fluorophores — pyrene, tamra and fluorescein — Margulies and Hamilton showed that five proteins, including the related avidin and streptavidin, could be detected and distinguished by monitoring changes in fluorescence.

The definitive versions of these Research Highlights first appeared on the *Nature Chemistry* website, along with other articles that will not appear in print. If citing these articles, please refer to the web version.

blogroll

Stanford stand-off

A rumble in the chemistry jungle and an elemental TV appearance.

A letter to *Chemical and Engineering News* (vol. 87, p5) from Carl Djerassi decrying the lack of credit given to Robert Pettit’s isolation of bryostatin in Barry Trost’s recent total synthesis paper has generated a lot of interest from the blogosphere. It started with Sam at Everyday Scientist (<http://tinyurl.com/dz7syh>), commenting that citing original work is important and wondering whether *C&EN* is the right forum, especially when there are other examples of inadequate citation. He was also a little confused because “the Trost paper does cite Pettit ... at least three times.” At The Chem Blog, Kyle Finchsigmate’s post (<http://tinyurl.com/afzh8w>) elicited a flurry of comments ranging from recipes for fried chicken (don’t ask) to more interesting discussions on whether research groups of 40 people are really workable. All this noise got picked up by Katharine Sanderson at the *Nature* blog The Great Beyond (<http://tinyurl.com/acq5t2>) — fittingly enough, as the paper was published in *Nature* originally. Maxine Clarke added some important extra detail in a comment: Djerassi wrote letters in support of Pettit to both *C&EN* and *Nature*, protesting against “a draconian closure of his laboratory” at Arizona State University.

Meanwhile, boron and its appearance on the Conan O’Brien TV show in the USA got a few bloggers sitting up. The new-found TV stardom follows from the discovery of its new form (see page 23 of this issue) and a write-up in the *New York Times*. The reporter (<http://tinyurl.com/dls7vg>) made a slight mistake in reporting the number of forms (three instead of four), sparking comedy routines on TV talk-shows. Sugar Daddy, on our very own Sceptical Chymist (<http://tinyurl.com/cavdrn>), describes how O’Brien “whipped out a big poster board with crystal structures of the various forms of boron”. Excimer, who actually works with boron compounds every day, gave his thanks to the TV schedulers on Carbon Based Curiosities (<http://tinyurl.com/deue85>).