

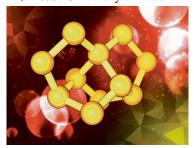
# **Swiss Science Concentrates**

**A CHIMIA Column** 

Short Abstracts of Interesting Recent Publications of Swiss Origin

## **Interfacial Synthesis of Trinorbornane**

Lorenzo Delarue Bizzini, Thomas Müntener, Daniel Häussinger, Markus Neuburger, and Marcel Mayor\*, *Chem. Commun.* **2017**, *53*, 11399. University of Basel



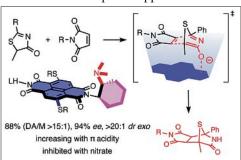
The Chemical Universe Database GDB, which was introduced by the group of J.-L. Reymond in Bern, aims to computationally define unknown chemical space by considering both chemical stability and synthetic feasibility of large numbers of potential

compounds. One appealing structure representing a simple, yet new structural type with no 'real-world' counterpart was tetracy-clo[5.2.2.0<sup>1.6</sup>.0<sup>4.9</sup>]undecane. Mayor and co-workers set out to synthesize this 'trinorbornane' which they could obtain in 7% overall yield in 9 steps, proving that the unique scaffold could indeed be brought from the realm of possibility into reality. The Mayor group is now exploring functionalized trinorbornane structures as well as synthetic routes towards enantiomerically pure samples of this tetracyclic hydrocarbon.

#### Anion– $\pi$ Catalysis of Diels–Alder Reactions

Le Liu, Yoann Cotelle, Anna-Bea Bornhof, Céline Besnard, Naomi Sakai, and Stefan Matile\*, *Angew. Chem. Int. Ed.* **2017**, *56*, 13066. University of Geneva

The relatively new anion— $\pi$  interactions have recently been employed in the area of asymmetric catalysis. Matile and co-workers have now employed anion— $\pi$  moieties in asymmetric cycloaddition reactions. Intramolecular Diels-Alder reactions are typically catalyzed by acids and generate mostly *endo* products. In contrast, bifunctional anion— $\pi$  catalysts composed of amine bases adjacent to the  $\pi$ -surface of naphthalenediimides were found to selectively stabilize the *exo* transition state on the  $\pi$ -acidic aromatic surface. The power of this approach was demonstrated by exo-specific, enantioselective Diels—Alder reactions of thiazolones and maleimides with complete suppression of the otherwise dominant

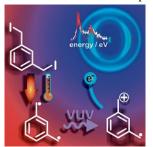


Michael addition. These anion— $\pi$  catalysts can therefore be added as a powerful accessory to the stalwart Diels-Alder reaction.

# Photoelectron Spectrum and Energetics of the *meta*-Xylylene Diradical

Mathias Steglich, Victoria B. F. Custodis, Adam J. Trevitt, Gabriel daSilva, Andras Bodi, and Patrick Hemberger\*, *J. Am. Chem. Soc.* **2017**, *139*, 14348. Paul Scherrer Institute, ETH Zurich, Uni. Wollongong, Uni. Melbourne.

From quantum chemistry to material science, aromatic diradicals' properties offer a wide range of potential applications. The electronic structure of the *meta*-xylylene diradical makes it one of the most interesting, albeit elusive, model systems to date. Hemberger and co-workers developed a powerful approach to generate and probe m-xylylene radicals. Using flash vacuum pyrolysis of the diiodo precursor, m-C $_8$ H $_8$ I $_2$ , they obtained m-C $_8$ H $_8$  in a molecular beam, which was probed by photoelectron spectroscopy in combination with mass spectrometry. Using this approach, they



elucidated electronic and vibrational features of m-C<sub>8</sub>H<sub>8</sub>, as well as thermochemical data including adiabatic ionization energies and enthalpies of formation. Their experiments suggest m-C<sub>8</sub>H<sub>8</sub> could dramatically alter the electronic and magnetic properties of a material, without necessarily affecting its structural features.

### **Olefins from Natural Gas by Oxychlorination**

Guido Zichittella, Nicolas Aellen, Vladimir Paunović, Amol P. Amrute, and Javier Pérez-Ramírez\*, *Angew. Chem. Int. Ed.* **2017**, *56*, 13670. ETH Zurich

Natural gas reserves are rich in ethane and propane, thus offering the potential to produce ethylene and propylene, the key building blocks for the manufacture of various polymers, pharmaceuticals, and fine chemicals. The current processes for the production of these olefins are unable to close the growing gap between demand and manufacturing capabilities. Pérez-Ramírez and co-workers discovered herein an exceptional europium oxychloride (EuOCl) catalyst for the one-step conversion of ethane and propane into olefins by oxychlorination chemistry, thus achieving high yields for ethylene (90%) and propylene (40%). Furthermore, EuOCl is able to process complex mixtures of alkanes, thereby reducing separa-

tion costs, and it maintains its performance for over 150 h under realistic process conditions. Oxychlorination thus offers a low-cost and highly scalable alternative to manufacture light olefins from natural gas.

