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Synthesis and Supramolecular Chemistry of 2,3-Bis(2,2'-oligopyridyl)pyrazines

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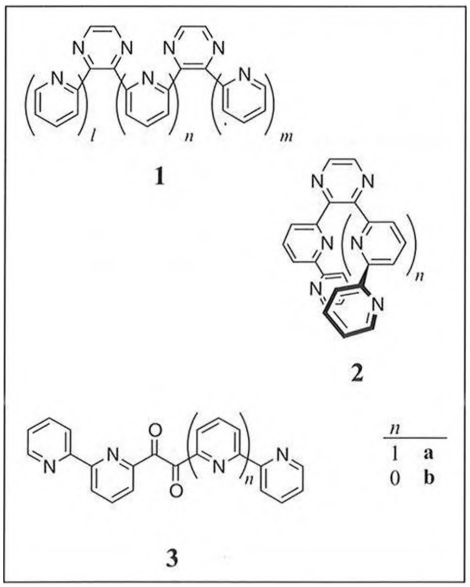
Abstract. Methods are being developed for the synthesis of pyrazine derivatives which are 2,3-disubstituted with 2,2'-oligopyridyl chains. We are currently investigating the supramolecular topology and complexation behavior of these novel compounds.These two aspects of their behavior appear to be largely determined by steric and electronic effects associated with the structure of the pyrazine ring.

Fenton Heirtzler was awarded a B.Sc. in Chemistry in 1985 at McGill University, Canada and an M.Sc. in Organic Photochemistry from Michigan State University in 1989. He received his Ph.D. in 1993 with *H. Hopf* in Braunschweig which was followed by two years of post-doctoral research in the group of *E. Constable*. He is currently working towards the completion of his Habilitation in Supramolecular and Synthetic Chemistry. Further information can be found at: http://ac.chemie.unibas.ch/~heirtzler.

Over the past three and a half years, my habilitation has addressed the preparation, characterization, and complexation chemistry of 2,6-oligopyridyl-2,3-oligopyrazines of the general structural formula **1**. What is so striking about this class of compounds? First, their synthetic novelty. Although oligopyridines have been a favourite motif in supramolecular chemistry for more than 16 years [1], only a handful of oligoheterocyclic compounds containing the pyrazine ring have been prepared and studied since the late 1950's [2]. The synthesis of most new oligoheterocyclic systems exploits mature synthetic methodologies, and so the paucity of such pyrazine-containing compounds may well be ascribed to the absence of specific studies directed toward their synthesis.

The preparation of both symmetrical and 'mixed' compounds, such as **2a** and **2b** from the corresponding oligopyridyl α-diketones **3**, is reasonable but complicated by the electron-withdrawing, potentially over-reactive and chelating nature of the oligopyridine starting materials. Thus, we have developed *de novo* approaches based on novel oxidation reactions – especially for the 'mixed' α-diketones – which allow access to a variety of oligoheterocyclic compounds, including some containing two pyrazine rings.



Our current research interests concern the consequences of the 2,3-disubstitution pattern around the pyrazine ring and the conjugative relationship between its N-atoms on both stereochemistry and complexation behavior. Some important questions include:

- The binding of one kinetically labile metal center to the pyrazine ring deactivates the binding of a second one; dimeric 'metallophanes', which engage in strong intra- and intermolecular π-stacking, are formed [5][6]. Can these findings be applied to the preparation of electrically conducting materials?
- Extensive through-space interaction occurs between adjacent appended oligopyridyl chains and twists them about one another. Are non-racemizable double-helical oligoheterocycles possible?
- Complexation of both pyrazine N-atoms with inert metal centers results in sterically hindered, metallo-organic helicenes [7]. Can enantiomerically pure compounds be prepared on this basis?

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