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Electrochemical Studies on C,N,S and C,N,Se Ring Systems—An Overview

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ELECTROCHEMICAL STUDIES ON C,N,S AND C,N,Se RING SYSTEMS - AN OVERVIEW

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Abstract Electrochemical studies of 5, 6, 7 and 8-membered rings containing catenated C-N-S and C-N-Se groups have been undertaken using cyclic and a.c. voltammetry. The results find a satisfying interpretation using semi-empirical MO theory. The results provide an important insight into the utility of such ring systems for the design of molecular metals.

ELECTROCHEMICAL STUDIES

1,2,3,5-Dithiadiazoles and diselenadiazoles, **1**, have been studied electrochemically starting from both the 6π cation (as the PF_6^- salts) and 7π neutral radicals (by dissolution of their dimers in CH_2Cl_2 or CH_3CN). The neutral dimers are the preferred starting compounds.¹ These rings demonstrate both reversible

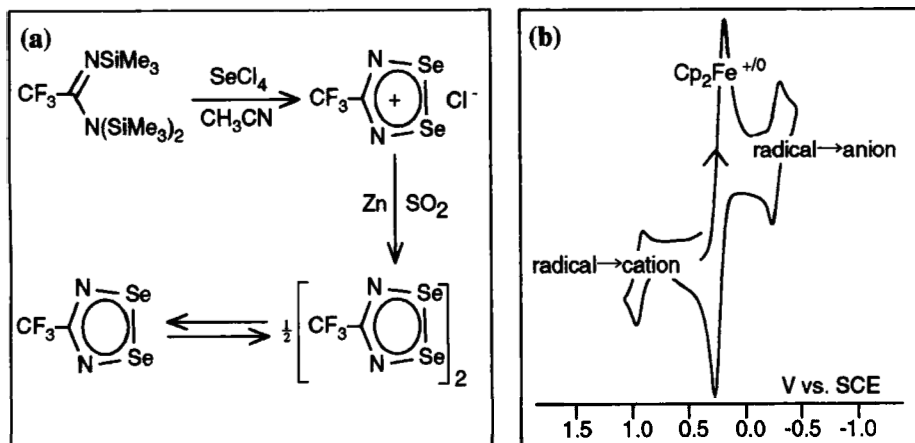
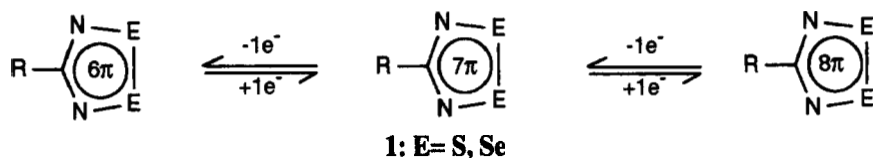
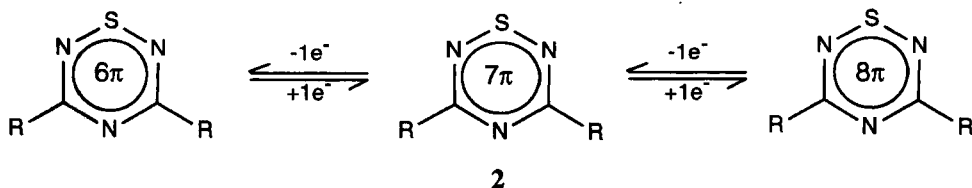


FIGURE 1 (a) Synthesis of $\text{CF}_3\text{CN}_2\text{Se}_2$; (b) cv in CH_2Cl_2 with reference

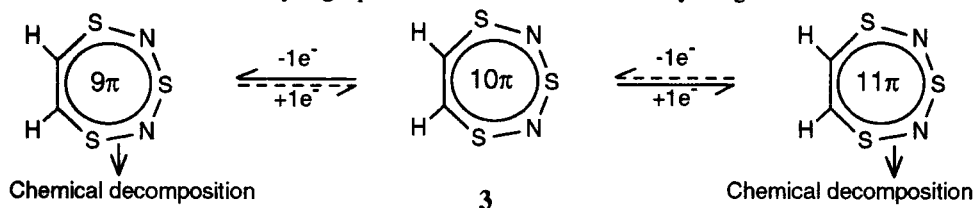
oxidation and reversible reduction (to the 8π anions) in almost all cases [$R=4-X-C_6H_4$, $X=MeO$, CH_3 , H , Cl , CF_3 , $E=S, Se$; $R=Me_2N$, CH_3 , H , Cl , CF_3 , $E=S$; $R=CF_3$, $E=Se$.] These rings can therefore exist in a triad of oxidation states, a requirement for their use in building molecular metals.

1,2,4,6-thiatriazines, **2**, can also exist in three stable oxidation states, and this has been verified electrochemically. The voltammograms clearly show the

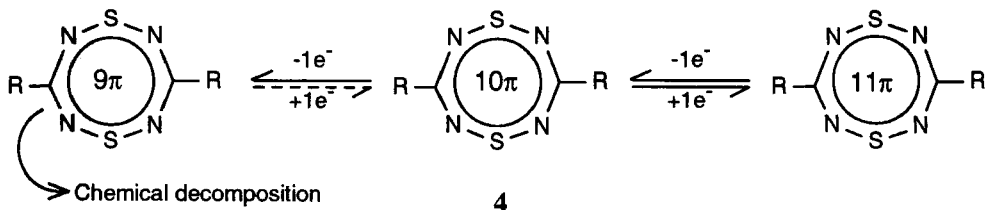


presence of both the monomer and the dimer of the 7π neutral ring system (whether or not we proceed from the PF_6^- salt of the cation or from the neutral dimer.)

1,3,5,2,4-trithiadiazepine, **3**, is a stable 10π aromatic heterocycle. It undergoes irreversible oxidation at +1.85 V vs. SCE and irreversible reduction to the 11π anion at the very high potential of -1.69 V, a stability range of 3.54 V.



1,5,2,4,6,8-dithiatetrazocines, **4**, are another example of a stable 10π aromatic ring system (so long as they bear aryl or alkyl substituents; the parent heterocycle is unknown.) They undergo irreversible oxidation to the 9π cation and



reversible reduction to the 11π anion.³

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