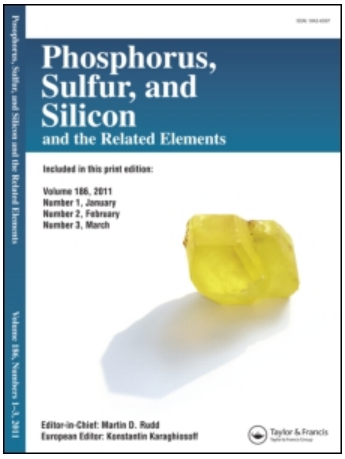

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Electrochemical Studies on C,N,S and C,N,Se Ring Systems—An Overview

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

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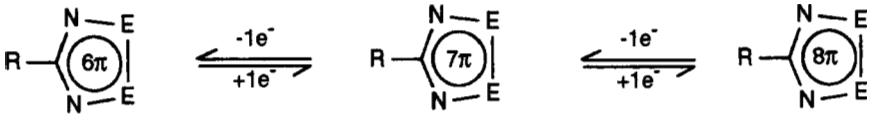
Abstract Electrochemical studies of 5, 6, 7 and 8-membered rings containing catenated C-N-S and C-N-Se groups have been undertaken using cyclic and a.c. voltammetry. The results find a satisfying interpretation using semi-empirical MO theory. The results provide an important insight into the utility 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 prefered starting compounds.[1] These rings demonstrate both reversible



1: E= S, Se

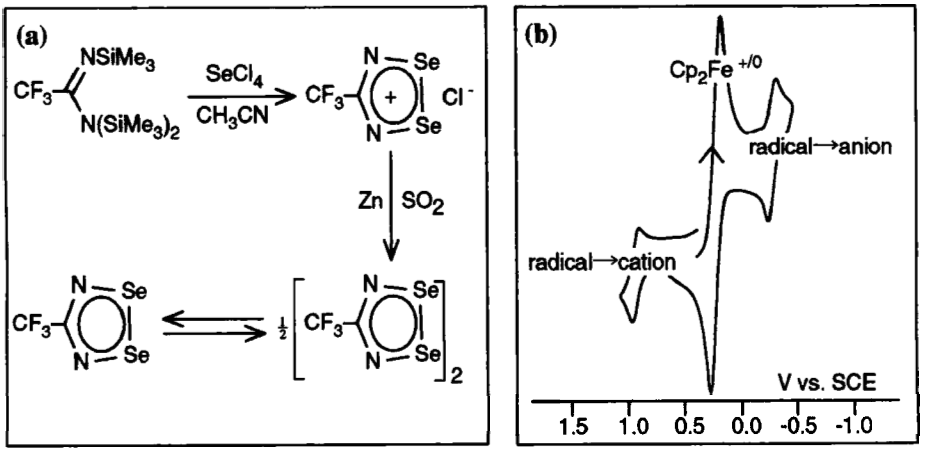
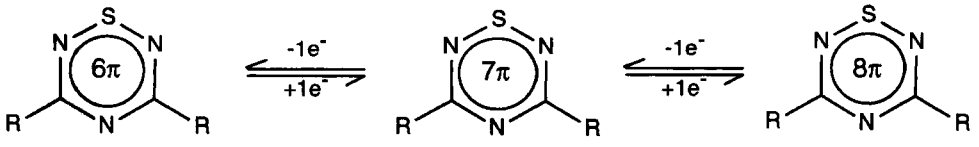


FIGURE 1 (a) Synthesis of $CF_3CN_2Se_2$; (b) cv in CH_2Cl_2 with reference

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.

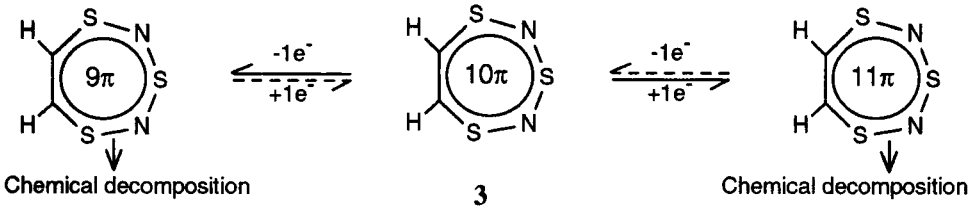
1,2,4,6-thiatriazines, **2**, can also exist in three stable oxidation states, and this has been verified electrochemically. The voltammograms clearly show the



2

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.



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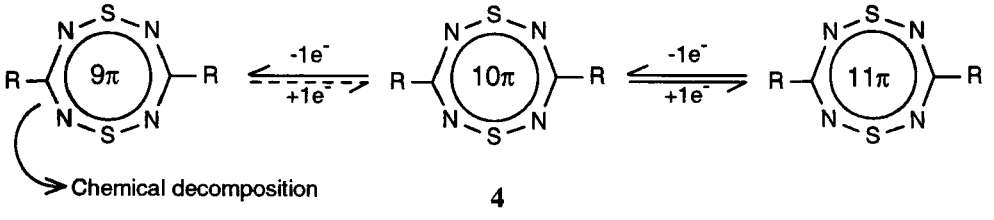
1,5,2,4,6,8-dithiatetrazocines, **4**, are another example of a stable 10π aromatic ring system (so long as they bear aryl or alkyl substituents; the parent heterocycle is unknown.) They undergo irreversible oxidation to the 9π cation and



4

reversible reduction to the 11π anion.[3]

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