Electrochemistry of Redox-Active Group 15/16 Heterocyles

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Abstract

This review is a critical overview of the literature on electrochemistry of unsaturated ring-compounds containing bonds between Group 15 and Group 16 elements (principally S and N), including metallacycles. It contains a detailed compilation of measured redox potentials and the conditions under which these were obtained for over 200 compounds. An introduction to the application of solution electrochemistry to this class of compounds is provided, and the relevance of such measurements to materials design is discussed.

Contents

1. Introduction and Scope

1.1 Introduction

Redox-active heterocycles are important to materials science and to biochemistry. Considerable advances have been made in the synthesis of heterocycles containing several Group 15 and 16 elements [1-4]. Heterocyclic thiazenes and selenazenes (including mixed S/Se species) are thought of as hybrids of aromatic or anti-aromatic hydrocarbons and binary sulfur or selenium nitrides. Such ring systems have been aggressively studied as possible candidates for molecular metal design [5]. Replacement of nitrogen by the heavier Group 15 elements has also been achieved in several cases [6]. Considerably less is known about the electrochemical properties of this large class of ring compounds, and electrochemistry has only recently been applied to this study in anything approaching a comprehensive manner. The purpose of this review is to provide a critical evaluation of the known electrochemical data, and their interpretation, with suggestions and directions for further study. We hope our efforts will encourage other workers to make greater use of electrochemistry in their research into a fascinating field of chemistry.

1.2 Focus: Radical ion conductors and neutral radical conductors

This review will focus on rings rich in Group 15 and/or Group 16 elements. We will not discuss the large number of studies treating ring systems important to biological chemistry. Leading references to this field, which include the elucidation of the mechanism of photosynthesis and nucleotide redox reactions are provided for the interested reader [7]. We will only treat the huge class of tetrathiafulvalene (TTF) related compounds in a peripheral fashion. The importance of electrochemistry in the design of conducting [8], and more recently superconducting [9], charge transfer compounds [10] has long been recognized. Similarly, electrochemistry has always been a standard tool in the investigation of narrow-bandgap conjugated polymers [11]. Instead, we will focus on less-well studied ring systems**, generally those with bonds between Group 15/16 elements incorporating unsaturation** [1].

The primary focus of this review will be rings, which are of interest in the development of entirely new classes of molecular metals or molecular magnetic materials. Research in this area can be broadly classified as that which deals (A) with *radical ion* conductors and (B) with *neutral radical* conductors. The first class has historically been dominant, and primarily includes TTF-TCNQ "charge transfer salts" (CT), for which literally thousands of variants both in the donor (TTF) and acceptor (TCNQ) have been synthesized and examined for conductive properties. However, it has now been very well established that the *acceptors* play no role in the conductivity of such salts, except as part of the general structure-determining components of the solid architecture. Indeed, the replacement of the TCNQ by inert inorganic anions led to the discovery of *superconducting* salts by Bechgaard, and such salts of TTF and TTF-derivatives such as the well-known ET are now commonly known as Bechgaard salts [12]. The term **radical ion conductor** (RIC) has recently been put forward as a general class descriptor for all such compounds in which a radical cation or radical anion species is created in some sort of solid-state lattice that allows for the migration of electrical charge through the lattice [13]. The main path of conduction is along the stack direction of stacked radical ions.

The concept of a **neutral radical conductor** (NRC) was first put forward by Haddon using odd-alternant hydrocarbons as a proposed model for a conducting system without the use of permanently charged radicals for the conduction pathway, thus avoiding the significant coulombic repulsion that accompanies the attempt to form conducting stacks of radicals [14]. Although much was learned from the odd-alternant hydrocarbons, and research is continuing in this area [15], the utility of such compounds is dramatically limited by a tendency to form strongly C-C bonded molecular dimers rather than infinite stacks of solid-state materials. Indeed the focus in this area has been to incorporate heteroatoms within and/or fused to, the hydrocarbons rings, and as such this area of research has tended to merge into the heterocyclic sphere that is the scope of this review. Recently *conducting* molecular solids have been obtained using spiro-biphenalenyls that use a borate structural core and no additional heterocyclic substituent [16].

As a part of our own approach, we have treated the electrochemistry of both the ring systems that are radicals (neutral or charged) of potential interest in conducting systems (those whose radical form lies closer to the centre of the redox spectrum) as well as the closely-related rings for which diamagnetic forms dominate at the centre of the redox spectrum, and whose redox active forms lie well to the anodic and cathodic regimes. It is recognized that these latter classes of compounds are useless for application to conductive systems, but nevertheless important lessons can be learnt for such ring systems with respect to (A) the width of the redox window and (B) the tunability of the redox states by ring substituents. Both these themes will be addressed in this review.

The greatest interest for applications to conducting systems are those species which have at least three redox states that are easily attainable and, preferably, reversibly interconvertible. Indeed Group15/16 heterocycles are one of the most abundant areas where such special properties are observable (outside this area are primarily transition metals with multiple redox states (such as Vanadium) or the recently identified redox isomers of the fullerenes.)

1.3 Solution measurements of the disproportionation energy

One of the chief design factors sought in both kinds of molecular metals (i.e. RIC's and NRC's) is weak electron-electron (coulombic) repulsion, since this can be correlated with minimization of ionic fluctuation during current flow through the solid. A chemical expression of weak coulombic repulsion is a low disproportionation energy, i.e. for the reaction:

$$2\ \text{Radical} \quad = \quad \text{Oxidized diamagnet} \quad + \quad \text{Reduced diamagnet} \qquad (1)$$

the unfavorable free energy should be *minimized*. An estimate of the size of this process in the solid state can be obtained from solution electrochemistry. The electrochemical cell potential, E_{cell} for reaction (1) has been obtained for classical charge-transfer type RIC's, for example the donor TTF for which E_{cell} ($2\ TTF^{\cdot +} = TTF + TTF^{2+}$) = 0.3 V [17], and the acceptor TCNQ for which E_{cell} ($2\ TCNQ = TCNQ^{\cdot -} + TCNQ^{2-}$) = 0.42 V [18]. Where appropriate in this review we have included the E_{cell} values obtained for the system-appropriate triad of oxidation states. The cell potential will always be expressed as a *positive* number, i.e. $|E_{process\ 1} - E_{process\ 2}|$, recognizing that this value is preferentially as small as possible for conducting systems. (In doing so, we are effectively using the so-called “European” sign convention for electrode processes [19].)

This E_{cell} value is numerically identical to the electrochemical estimate of bandgap, which has been used extensively to characterize small-bandgap conjugated polymers. In such polymers, the estimation of the actual bandgap of the polymer (E_g) from the solution oxidation (E_{ox}) and reduction (E_{red}) potentials has been facilitated with the help of the empirical equation:

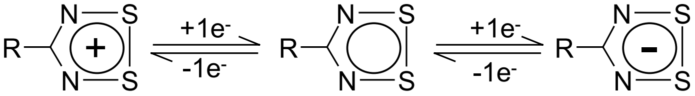
$$E_g = (E_{ox} - E_{red}) + (S^+ + S^-)\left[1 - \left(\frac{1 - \frac{1}{\varepsilon_2}}{1 - \frac{1}{\varepsilon_1}}\right)\right] \qquad (2)$$

where S is the solvation energy of the ionized molecule minus the solvation energy of the neutral molecule and ε_1 and ε_2 are the dielectric constants of the solution and the solid, respectively [11]. Nothing approaching this level of sophistication has been attempted for potential molecular metals, perhaps in part because of the impossibility of predicting the solid-state packing of the molecules which has a huge importance since without appropriate packing the long-range overlap necessary for conduction is simply absent. Nevertheless, the concept of measuring the HOMO-LUMO gap from electrochemistry is generally useful, and we have thus included $|E_{cell}|$ values for all rings for which at least two complementary redox processes have been measured. While the numerical value of this measurement is unchanged, we wish to point out that these $|E_{cell}|$ values only correspond to disproportionation energies when the conditions of Reaction (1) are fulfilled.

In addition to this important cell potential, classical charge-transfer salt research has long had "electrochemical recipes" for various CT systems. Thus, for example, donors towards the acceptor TCNQ need to have values for the 0/+1 process between +0.5 and 0.0 V [8]. Similar criteria can be established for any particular acceptor system. While the importance of such criteria have been diminished since the development of inert anions for RIC's, the simplicity of forming and testing charge transfer salts with acceptors like TCNQ continues to appeal to the molecular metal design community [20].

1.4 Organization of the review

The data has been organized into comprehensive data tables, which are located at the end of the review. In order to try and remove the ambiguity that surfaces precisely because redox active heterocycles can often be prepared in more than one redox state, the data has been organized by **redox process**. Each process is presented as a redox couple, starting with the most negative oxidation state, and proceeding to the more positive. The overall charge on the molecular species is used to identify the oxidation state, and the process may be a one, two, or greater, electron process. Thus –1/0 identifies a one-electron process corresponding, under reversible conditions, to either the reduction of the neutral species, or the oxidation of the mono-anion. We will avoid the terms "oxidation" or "reduction" from our discussion as much as possible to avoid confusion, and instead specify redox couples. The definition is illustrated by the following example:



This triad of redox states is inter-converted by the redox processes –1/0 and 0/+1. Effectively our method boils down to using the so-called "European" sign convention for electrode processes (see section 1.3). However, additional complexity is introduced by the specific electrochemical technique employed to measure the cell potentials. For reversible couples the potentials will be the same irrespective of the starting material used, but since not all processes are reversible, the actual identity of the bulk material in the electrochemical cell is indicated for each measurement. When measurements have been performed on more than one oxidation state of a given ring system this is indicated, but the system is assigned only a single identification number. Structural diagrams are provided in the data tables and will not as a rule be duplicated in the body of the text in order to save space.

The first table presents electrochemical data for several relevant benchmark compounds. These include TTF and TCNQ, the original components of CT salts, some common aromatic hydrocarbons, and simple heterocycles which are *not* included in the review precisely because they undergo electrochemical polymerization reactions. The remaining tables are primarily organized by ring size, and secondarily by the location of the Group 15 and 16 elements in the ring. The remaining ring atoms are usually carbon, but also include iso-electronic equivalents to C such as R_2P and O_2S^-. Metallacycles are grouped together at the end.

1.5 Ring sizes included

The data is organized by ring size, with the exception of Table 2, which deals with all sizes of binary S,N rings and cages, and the tables of metallacycles and miscellaneous rings, which are at the end. Little is known about four membered unsaturated Group 15/16 rings. The benzothiazetes once claimed [21] have been shown to be fused five-membered dithiazole ring systems [22].

The majority of results have been obtained on five membered rings, including many ring systems fused to benzenoid aromatics, and many non-fused rings such as the dithiadiazole system, which can bear a wide variety of substituents at carbon. Less is known about six-membered rings, which include the thiatriazine and dithiatriazine ring systems. Very little is known on seven-membered rings, while the eight-membered dithiatetrazocine ring system has been studied in two different structural modifications.

2. Methodology

2.1 Electrochemical techniques, solvent and electrolytes

The earliest studies consulted in the preparation of this review emphasized electrochemical reduction, and used polarography (P) overwhelmingly [23]. More recent work has tended to use cyclic voltammetry (CV), and work in both oxidizing and reducing regimes [24]. Except for the earliest work, in which protic solvents were common, the majority of the data has been recorded in aprotic non-aqueous solvents, of which acetonitrile (CH_3CN) is the most common. Other solvents which have been used are dichloromethane (CH_2Cl_2), 1,2-dichloroethane, dimethylformamide (DMF), trifluoroacetic acid and sulfur dioxide.

To date no results have been published in the less-polar solvents which have become accessible in recent years with the introduction of specialized electrolytes or through the use of microelectrode techniques in the absence of supporting electrolyte [25,26]. Recently, 1,2-difluorobenzene has been proposed as a useful electrochemical solvent for transition metal complexes, but none of the data in this review was obtained in this solvent [27].

The importance of solvent effects has recently been emphasized by careful comparative work in more than one solvent. Thus for the 1,2,3,5-dithiadiazole ring system it has been demonstrated that, starting with the neutral radicals in solution, the $E_{½}$ for the 0/+1 process differs by ~0.2 V between CH_3CN and CH_2Cl_2, while the –1/0 wave is almost unaffected by the change in solvent [14,28]. It is obvious that the comparison of data obtained in different solvent systems should be practiced with caution, and the same probably applies to different electrolyte systems as well. Early work in protic solvents was rendered unreliable by redox-induced degradation reactions involving the solvent medium. As a rule compounds containing bonds between the Group 15/16 elements are susceptible to hydrolysis, so protic solvents should be avoided to suppress decomposition reactions, and carefully dried solvents should be used at all times.

2.2 Referencing

The correct referencing of electrochemical data has always been troublesome. There is no universal consensus as to which reference system to use, and in this Review we have elected to report the data as presented in the original reports. However, sign conventions have been corrected to the so-called “European” convention, in which the sign of an electrode process is an *invariant* quantity [19].

Bond has argued convincingly that internal referencing is to be preferred in all cases, and even goes so far as to quote his data against the Fc^+/Fc couple as zero [29]. Indeed a position paper has been adopted by the Commission on Electrochemistry of the IUPAC suggesting that internal referencing to the Fc^+/Fc couple should be used in all voltammetric measurements [30]. The advantages of using an internal reference are obvious, both from the view of accuracy (errors due to the effects of junction potentials and differences in solvent and electrolyte) and convenience (complexity in the construction of cells that handle highly sensitive chemicals and/or operate under pressure or vacuum.)

We are not convinced, however, that changing the zero on the reference scale to the potential of the Fc^+/Fc couple is wise. The vast majority of the data for organic polarography and cyclic voltammetry is reported against the saturated calomel electrode (SCE), usually in a half-cell containing the same solvent and electrolyte system as the working half-cell. Despite all difficulties caused by changes in solvent system, junction potentials and the like, it is still often desirable to compare two different values measured in different experiments and obtain a first approximation as to the relative redox power of a given redox couple. It is for this reason that we prefer carefully calibrated corrections to the established external SCE scale. (This corresponds to the very common practice in NMR of converting chemical shifts from a variety of internal reference compounds to a *single* zero point for the scale of a given nucleus.)

In our own work we have elected to use single-compartment three-electrode system with a pseudo-reference electrode, and using an internal standard for the redox potentials [14,28,31-35]. These standards are calibrated in careful measurements against the SCE, and the potentials are then converted to the SCE scale. The most commonly used internal redox reference is the ferrocene/ferrocenium couple (Fc/Fc^+), which with 0.1 M $N^nBu_4PF_6$ (TBAFP) appears at +0.38 V vs. SCE in CH_3CN solution, and +0.48 V in CH_2Cl_2 [28] [36]. Other workers have determined this couple in CH_3CN solution as +0.31 V by polarography at the dropping mercury electrode or +0.307 V by chronopotentiometry at a mercury pool electrode using $LiClO_4$ as the electrolyte [37] or +0.40 V at a Pt electrode also using TBAFP [38]. Such variability is precisely the reason that internal referencing should be used. A given cell-electrode-electrolyte-solvent combination should be carefully referenced against an external SCE to calibrate the scale as accurately as possible, taking pains to minimize the junction potential between the aqueous and non-aqueous solvents; however precision of greater than ±0.1 V cannot be expected in general due to the *many* variables involved.

The accuracy of our approach has been substantiated by the nearly identical potential values for a series of 1,2,3,5-dithiadiazole rings obtained by this method compared to measurements made on the same compounds in a two-electrode cell using a pressure-equalized Ag/Ag^+ reference electrode, which was itself calibrated externally to an SCE electrode [39]. Other internal redox standards that can be used (e.g. if the ferrocene couple blocks the region of interest, or the solvent used is not stable at ~ +0.5 V) in acetonitrile or methylene chloride solution in conjunction with TBAFP are $[N^{n}Bu_4]_2[IrCl_6]$ (two reversible couples in CH_2Cl_2 at –0.02 V and +1.74 V vs. SCE) and $AgPF_6$ (in CH_2Cl_2 +0.38 V vs. SCE) [36].

There is no doubt that the SCE scale has been the dominant one in use by the molecular metal and small band-gap polymer community. Kaplan, et al. indicated that redox potential measurements on this scale for classical CT components have proven to be extremely repeatable where the same compounds were deliberately re-determined in several laboratories over a wide time and geographic spread [18].

2.3 Specialized electrochemical cells

The study of redox active heterocycles requires, from time to time, the handling of high concentrations of free radicals in solution. In addition, many Group15/16 linkages are highly susceptible to hydrolysis by adventitious moisture. Also, some binary Group 15/16 compounds are freely soluble only in exotic solvents such as sulfur dioxide. Thus progress in electrochemistry on these compounds has depended on the development of specialized electrochemical cells. Two examples of specialty cells that have been used to advantage are described here.

A cell developed for handling very air-sensitive inorganic materials has been described [40]. A diagram of this innovative cell is reproduced in Figure 1a. This design uses break-seal technology to produce an all-glass cell (except for a single Teflon rotary stopper). During cell operation, the electrolyte and solvent are first introduced into the working compartment to obtain background scans and measure the actual available solvent window. The analyte is then introduced by washing the contents of the first break-seal into the working cell, and later the internal reference can also be added in the same way. It is even possible to add the analyte and/or reference in portions to prevent one or the other from swamping the signals. The internal coldfinger allows the experiment to be cooled below ambient temperature. This cell can also operate under mild pressure, e.g. using sulfur dioxide as the solvent.

Insert Figure 1 here

A second design, but one using an ingenious, though complex, Ag/Ag^+ reference electrode, was initially developed for sulfur dioxide solvent work at ambient temperature [39]. It has since been used in numerous studies using the more conventional solvent CH_3CN, in which the ability to load the cell in the glove box was advantageous for the handling of very air-sensitive compounds [41,42]. A diagram of this cell is reproduced in Figure 1b. Although this cell is compact and robust, it does not allow for solvent/electrolyte background measurements before analyte is added, nor for separate introduction of analyte and internal reference, and it has apparently always been used with a separate reference electrode compartment. The latter has been improved upon since the original report [42].

3. Benchmark studies

We briefly review the electrochemistry of some compounds that will help to set the context for our discussion on Group 15/16 heterocycles. First we consider come examples of aromatic hydrocarbons and heterocycles (see Table 1), and then what little is known about the electrochemistry of the binary thiazyl and selenazyl compounds (Table 2).

3.1 Aromatic ring compounds

It is well known that polycyclic aromatic compounds can be chemically or electrochemically reduced, often forming stable radical anions. Under some circumstances, they can also be reversibly oxidized. Benzene itself has a very large redox stability window (comparable to the E_{cell} values of redox-active compounds), that stretches from approximately –3 to +3 volts. It is thus decidedly redox-inactive. However, as the number of conjugated rings are increased, an ever-smaller separation between the reduction and oxidation potentials is observed, and this has been correlated to both the raising of the HOMO and lowering of the LUMO. Thus the redox stability window of naphthalene (**2**) is 4.04 V in acetonitrile [43], while that of anthracene (**3**) is only 2.87 V in the similar solvent DMF [44]. In particular the redox properties of anthracene mimic those of several heterocycles to be considered later. Compared to these carbacycles, heterocycles such as **5** - **7** have decidedly smaller redox stability windows, and indeed these are redox-active ring compounds (see below).

3.2 Classical charge transfer compounds

There continues to be intense efforts in CT salt development, almost all based on derivatives of tetrathiafulvalene (TTF, **3**) as the donor, either with acceptors derived from tetracyanoquinodimethane (TQNQ, **4**), or with redox-inert inorganic anions. The 0/+1 redox process for **3** is facile at +0.33 V, and the radical cation is a stable species that has been intensively studied. The second redox couple, +1/+2 occurs at +0.70, so that E_{cell} for **3** is 0.37 V, a small value, and one that is indicative of the types of E_{cell} required for molecular conductors. Similarly the acceptor has two facile reductions, the –1/0 couple at +0.18 V and the –2/–1 at –0.37 V, resulting in E_{cell} = 0.55 V. As previously mentioned, it has been found that in order for a donor to react spontaneously with TCNQ, it needs to have its 0/+1 redox couple within the narrow range of +0.5 to 0.0 V vs. SCE [8].

Several of the acceptors currently under development incorporate Group 15/16 heterocycles, and these will be considered in section 4. We are not able to include the numerous studies dealing with TTF derivatives within the scope of this review, and the reader is asked to consult the following leading references to this field [45-47]. Much of the most recent work seeks to incorporate TTF-like fragments into macromolecular assemblies. The goal of this work is the development of molecular electronic devices.

3.3 Small bandgap polymers from electropolymerization

When aromatic, or pseudo-aromatic, heterocycles such as pyrrole (**5**), indole (**6**), thiophene (**7**) or thianaphthene (**9**) are electrochemically oxidized, they polymerize and often deposit a polymeric film right on the electrode surface. Such reactions have been dubbed $E(CE)_n$ reactions [48]. The films are found to be electrically conducting, and belong to the class of small-bandgap • -conjugated polymers. Some of the earliest recognized • -conjugated polymers were polyacetylene [49,50], $–(CH)_x=$, and polythiazyl (polysulfur nitride), $–(SN)_x=$ [51], clearly showing the heritage of redox active Group 15/16 heterocycles which have long been sought as the "missing link" between the "organic" and the "inorganic" branches of molecular material design [52].

All of these compounds are irreversibly oxidized because they form polymers, and it is possible to follow this process by CV until, as the film gets sufficiently thick, a limiting voltammogram corresponding to the polymer is achieved. It is equally possible to prepare and then polymerize oligomers such as the dimeric 2,2'-bithiophene (**8**) and the pentameric analogue (**10**) [48]. In this manner, various pendant side-groups, including other heterocyles, can be incorporated into the polymeric structure. Notice also that **10** is sufficiently large to be able to demonstrate reversible 0/+1 and even a second +1/+2 redox couple. An oligomeric system similar to **10** has recently been studied, with indications that conduction along the • -stack is an important part of the conductivity of this system, and thus possibly also in the oxidatively doped polymers [53]. The extensive work in this field has been comprehensively reviewed [11], and will not be further discussed here. It suffices to say that small heterocycles with low Group 15/16 inclusion form oligomers and polymers when oxidized at mild potentials [48].

3.4 Binary S,N Compounds

Much of the driving force behind the development of binary S,N chemistry was provided by the unique conducting and super-conducting properties of polymeric thiazyl, $(SN)_x$ [51]. To this day $(SN)_x$ stands alone as a conducting polymer that does not contain any carbon, and unique as a non-metallic super-conducting polymer. Small ring systems containing only S and N were studied electrochemically several years ago [39,54,55]. The results are summarized in Table 2. A motif of the redox chemistry of this system is irreversibility, primarily because redox changes invariably induce molecular re-arrangements in these systems. The key result to note is that despite the fact that binary S,N compounds are formally electron rich, they are also good electron acceptors, and are thus comparatively easily reduced. Consequently, there is a large class of anions of binary sulfur nitrides, whose chemistry has received considerably study [56].

The simplest binary sulfur-nitride is the four-membered ring compound S_2N_2 (**11**) [57]. The 0/+1 couple measured by cyclic voltammetry (CV) occurs at +0.1 V in MeCN, and the –1/0 couple at –0.85 V. The cage compound S_4N_4 (**12**) has been studied both by CV and polarography (P) [54,58]. CV at Pt electrodes shows a quasi-reversible –1/0 couple at –0.43 V in MeCN solution at low temperature; a considerably more negative potential was reported by polarography at the dropping mercury electrode (DME). In-situ electron paramagnetic resonance (EPR) studies indicate that the product of the –1/0 couple is the $S_4N_4^{\bullet-}$ radical anion (9-line with $a_N = 0.12$ mT) [58]. At ambient temperatures the radical ion degrades rapidly to $S_3N_3^-$. Polarographic studies have identified two subsequent reduction steps (a) $S_4N_4^{\cdot-} + e^- \rightarrow S_4N_4^{2-}$

and (b) $S_3N_3^-$ + $2e^-$ $S_3N_3^{3-}$ [54]. Exhaustive electrolysis at –2.8 V results in the transfer of eight electrons and the formation of SN_2^{2-}.

The two-electron –1/–3 couple in Me_4N^+ salts of $S_3N_3^-$ (**13**) was found to occur at –2.5 V by polarography in separate experiments [54] (this value is given as –2.6 V for an unspecified salt in ref. [59]). The oxidation of *bis*triphenylphosphineiminium (PPN^+) salts of $S_3N_3^-$ in CH_2Cl_2 (–1/0 couple) was found to be reversible at RT by CV [55]. BF_4^- and $FeCl_4^-$ salts of the heart-shaped $S_5N_5^+$ cation (**14**) have been studied by different workers using CV [39,60]. The 0/+1 couple was reported to occur at +0.19 V {quasi-reversible (QR) at low temperature}or +0.06 V in CH_3CN and +0.46 at all temperatures in CH_2Cl_2, each measurement being performed on a *different* salt of the cation. A similar ~0.2 V solvent dependence with methylene chloride being more cathodic has been observed for 0/+1 couples in the 1,2,3,5-dithiadiazole system (see below).

The cage compound $S_4N_5^-$ (**15**) undergoes the –1/0 process at –0.12 V, while a further two-electron reduction was reported at –2.1 V (–3/–1 couple), as determined by polarography [54]. CV studies, on the other hand, identified a –2/–1 couple with the production of $S_4N_5^{\cdot-}$ whose identity was confirmed by EPR (triplet of 9 line patterns with a_N = 0.175 and 0.05 mT) in which the spin density is primarily delocalized over the four equivalent nitrogen atoms [61]. Oxidation of the initial salt produced S_5N_6.

A variety of oxygen-substituted S,N rings and cages (**17 - 19**) have also been studied by polarography [62]. For each class of compound, the reduction (usually a –3/–1 couple involving two-electron transfer) was found at considerably more anodic peak potentials than those of the corresponding binary compound (e.g. $S_3N_3O^-$ vs. $S_3N_3^-$). This has been explained by a lowering of the LUMO energy when the electronegative oxygen atom is attached to a sulfur-nitrogen ring or cage [62].

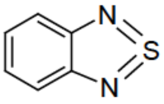
The predominant theme in the electrochemistry of the binary S,N compounds, however, is the instability of the species formed upon electrochemical oxidation or reduction. Only quasi-reversible behaviour is observed by cyclic voltammetry and polarography, and then usually only at reduced temperatures. Binary sulfur nitrides are highly susceptible to structural changes when their electron count is altered; electrochemistry merely confirms facts already known from chemical redox reactions [1,63]. By far the most important of such redox-induced changes is the preparation of the conductive polymer poly(thiazyl), $(SN)_x$ and its oxidatively doped derivatives. Electrosynthetic routes to polymeric thiazyl in doped and undoped forms have been reported [39].

4. Five-membered ring systems

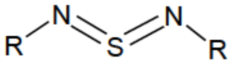
As mentioned under 3.3 above, most simple five-membered heterocycles undergo oxidative polymerization. The tendency to polymerize, or even to dimerize, upon oxidation or reduction is a common theme in carbocyclic redox chemistry. The effect tends to be minimized by higher Group 15/16 content, where polymers are as yet unknown. However as will be seen, simple dimerization is often observed. The data for this section is found in Table 3 (thiadiazoles and selenadiazoles), Table 4 (dithioles), Table 5 (1,2,3-dithiazoles and selenium containing analogues), Table 6 (1,3,2-dithiazoles and selenium containing analogues), Table 7 (1,2,3,5-dithiadiazoles) and Table 8 (1,3,2,4-dithiadiazoles). Five-membered heterocycles have been by far the most studied ring size, and these tables contain both compounds that are diamagnetic in the neutral state (thiadiazoles) and those that are paramagnetic in the neutral state (the rest of them). The dithiazoles have been reviewed recently, including some of the electrochemical data [4], as have the dithiadiazoles [64].

4.1 Thiadiazoles and selenadiazoles

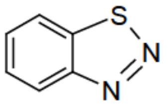
The data are in Table 3. The vast majority of this electrochemical data have been obtained on 2,1,3-thiadiazoles fused to aromatic rings, i.e. those systems bearing an –N=S=N– linkage. This is the well-known sulfur diimide group, which is also known as a linear chain compound outside of a heterocycle. It is a very stable group, and its redox chemistry [65] and reactivity [66]have been studied for the acyclic case. Far less is know about the electrochemical behaviour of the 1,2,3- isomers which have an –S–N=N– linkage. A great deal of interest in this system stems from its superb electron acceptor character, and it is a powerful substituent used for the modification of aromatic electronic structure in several branches of materials design [20,67-70].



2,1,3-thiadiazole

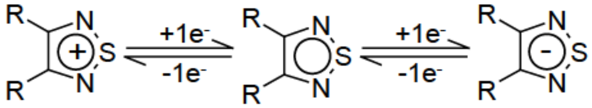


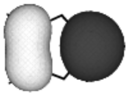
sulfur-diimide

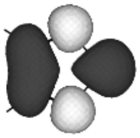


1,2,3-thiadiazole

Thiadiazoles are 2*N*+2 ring systems in the neutral form (the –N=S=N– unit contributes four •-electrons. Thus they are not capable of being used in the design of neutral radical conductors (NRC's). The redox processes examined by electrochemistry correspond to the following:



•-HOMO: 

•-LUMO: 

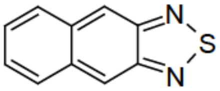
The redox couple corresponding to the 0/+1 process involves removal/addition of electrons from the • -HOMO of the neutral thiadiazole, while the –1/0 process involves addition/removal of electrons from the • -LUMO.

Simple thiadiazoles are also extremely stable towards both oxidation and reduction, as are all simple aromatic ring systems. This is easily seen from the large electrochemical stability window of **20**, for which the 0/+1 process occurs at +2.2 V and the –1/0 at –1.51 V (a 3.7 V window; compare ~6V in benzene, 4.04 V in naphthalene (**1**) and 2.73 V in anthracene (**2**)). However, the thiadiazole group has been a useful substituent in the construction of both donors *and* acceptors for radical ion conductors (RIC), as discussed below.

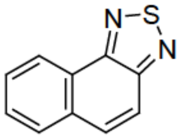
Both thiadiazole and selenadiazoles have been measured by electrochemistry; to date there seems to be no electrochemical data on telluradiazoles, perhaps because of their low solubility [71]. By comparison of analogous S and Se compounds in Table 3, e.g. **33** and **34**, **38** and **39**, etc. the –1/0 process is on average +0.08 V more anodic. A similar influence was observed in a careful comparative study of related dithia- and diselenadiazoles, for which the same process was observed to be ~0.2 V more anodic for Se vs. S [14]. This works out to ~0.1 per chalcogen, so is in fact very comparable.

The observed potentials for a given process for the fused-ring thiadiazoles included in Table 3 are found to be extremely dependent on structure because of differences in the amount of aromatic stabilization. Thus the –1/0 process for **23** is about 0.5V more cathodic than in the isomeric **24**. This can be rationalized using the extreme resonance forms for **23** and **24** shown below. Such differences are well known in heterocyclic aromatic chemistry, as seen for example in the huge difference in stability of naphtho[1,2-c]furan **a** and naphtho[2,3-c]furan **b** [72], also shown below for comparison.

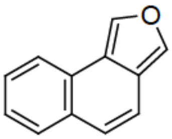
23



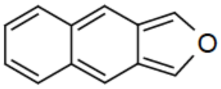
24



a



b



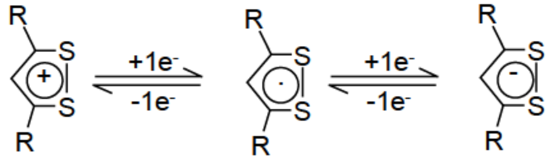
Yamashita, et. al., have shown that thiadiazole substituents are extremely effective in the construction of strong acceptor molecules for charge-transfer salt applications [20,67-69]. Thus compounds **27**, **28**, **29**, **30** and **36** are modified analogues to TCNQ, and are more powerful acceptors than the parent. The selenadiazole **28** has the most anodic $E_{½}$ at +0.04 V vs. SCE in acetonitrile solution of this series of compounds. The solution disproportionation energy of this series (i.e. for their radical anions) is extremely small, ranging from –0.17 to –0.56 V.

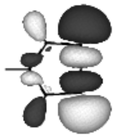
The effect of electron delocalization referred to above for **23** is emphasized in the disubstituted thiadiazole **35**, which has the most anodic –1/0 couple at +0.10 V, despite the fact that it has no dicyanomethane groups at all. Instead it has complete quinoidal electron delocalization within the three fused rings that make up this structure. A drawback to the use of this smaller molecule as an acceptor in actual charge transfer salts is the rather high E_{cell} value of –0.92 V. It should be noted, however, that since the recognition that the conductivity in most charge transfer salts is exclusively through the donor radical cation stacks, the relevance of a small disproportionation energy for the *acceptor* is less obvious [12].

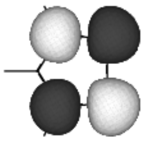
At the same time, the antiaromatic 12• dimethylpyrazine-based thiadiazole **31** acts as a powerful electron donor, with the 0/+1process occurring at +0.15 V vs. SCE. It forms conducting charge transfer salts with the acceptors **27, 28** and **29**, in which *both* radical cation and anion bear thia- or selenadiazole substituents.

4.2 1,2-Dithioles

1,2-Dithioles, by virtue of incorporation of two Group 16 elements into the ring, have an odd electron count in the neutral form. Not surprisingly, they are normally prepared as salts of the diamagnetic cations, as can be seen from the list of compounds included in Table 4. The exception is the fused-ring example **51**. They can therefore exist in a triad of oxidation states, interconverted as shown in the following graphic:



Possible • -SOMO 

Possible • -SOMO 

For this odd-electron species, oxidation involves the removal of electrons from the SOMO, while reduction adds an additional electron to this same orbital. For this ring system, two orbitals are very close in energy, one a strongly S–S antibonding • orbital, the other a weakly antibonding • -orbital, as shown above. At the AM1 level, the balance in energy slightly favours the indicated • -orbital as the true SOMO. For our purposes, this only means that the *possibility* exists that the –1/0 process may involve S–S scission.

We consider first the 3,5-disubsituted-1,2-dithioles (**41** to **50**), which are the subject of a careful comparative electrochemical study under identical experimental conditions, and for which CV has been undertaken in both methylene chloride and acetonitrile solution [73]. It is found that rings of this type tend to dimerize in the neutral radical form through the 3,5 C atoms [73]. Such dimerization is suppressed when the R group has significant steric bulk. Thus **46** and

50, which have at least one R = Me, demonstrate irreversible 0/+1 couples attributed to rapid dimerization at the C to which the Me group is attached. With bulkier aryl groups the 0/+1 couple is reversible at RT, but for example in **41** this process becomes completely irreversible at low temperature (–60°C), demonstrating a temperature dependence on the dimerization of the neutral free radical. In acetonitrile only the diaryl-substituted compounds (**41 - 45**) undergo two further reductive processes, identified as the –1/0 and the –2/–1 redox couples. A typical CV for this system is shown in Fig. 2. The original figure in reference [73] displays an erroneous scale; this has been corrected in our Fig. 2.

Insert Fig. 2 here

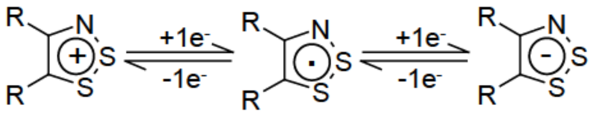
In these compounds, the central –1/0 redox couple is a very clear example of the condition of *electrochemical irreversibility with chemical reversibility* (EI-CR). The explanation put forward is that the mono-anion formed in **41** at –1.07 V rapidly cleaves its S–S bond to form a sulfido-thioketone. This species can then be further reduced by the –2/–1 process at –1.7 V to a disulfido species (the di-anion). The re-oxidation of the mono-anion only occurs at the much more anodic potential of –0.35 V. The condition for EI-CR is only met when the chemical change (in this case S–S bond cleavage) occurs much more rapidly than the cycling rate of the voltammetric experiment. We note that this cleavage is fully consistent with occupation of the strongly S–S anti-bonding • -redox MO shown above. It is interesting to note that for the 1,2,3,5-dithiadiazole ring system, AM1 calculations indicate that the redox MO strongly resembles the alternate • -SOMO shown in the scheme above; consistently there is no evidence for S–S bond cleavage attending the –1/0 redox couple for this ring system (see below).

Recently a fused-ring benzodithiolium heterocycle, bearing an extremely bulky 2,4,6-triisopropylphenyl substituent, has been isolated as the BF_4^- salt of its cation *and* has been isolated in the neutral radical form as a green solid. The EPR spectrum obtained from solutions of this solid fit an unassociated benzodithiolium radical, but the material has not been characterized in the solid state. A single redox process has been measured in this system whose potential matches closely that of the 0/+1 process of **49** [74].

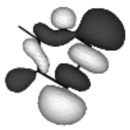
In contrast to the isolated 1,2-dithiole rings, the fused-ring examples **51** and **52** have reversible –1/0 couples. This has been attributed to the chemical rigidity imposed on these rings by the naphthalene and phenalenyl carbocycles: even if S–S cleavage were to occur in this system, the atoms would be held in close proximity so that the thermodynamics of re-oxidation would be unaffected by this change [75].

4.3 1,2,3-Dithiazoles and 1,2,3-diselenazoles

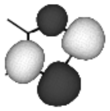
The 1,2,3-dithiazole and analogous diselenazole is an old ring system that has recently been vigorously re-investigated (see the references in Table 5). Unlike the thiadiazole and selenadiazole system, the incorporation of *two* Group 16 elements in a five membered ring leads to an odd-electron count in the neutral form. Thus dithiazoles are candidates for the construction of NRC's, if they can be stabilized in a triad of oxidation states, cation, neutral and radical, as shown below:



Possible • -SOMO



Possible • -SOMO



Again, since this is an odd-electron species, oxidation involves the removal of electrons from the SOMO, while reduction adds an additional electron to this same orbital. For this ring system, as for the 1,2-dithioles (section 4.2), there are two orbitals that are very close in energy, one a strongly S–S antibonding • orbital, the other a weakly antibonding • -orbital, as shown above. Again, at the AM1 level, the balance in energy slightly favours the indicated • -orbital as the true SOMO. Thus we again need to consider the *possibility* that the –1/0 process may involve S–S scission.

To date metallic conductivity has not been demonstrated for mono-substituted examples, but considerable progress has been made for di-substituted derivatives, which also have the restriction lifted of the neutral state having to be a radical. Early work on this system by the group of B. Strelets in Russia used polarography in acetonitrile [76,77]. Whether due to the affinity of sulfur for mercury, or whether these workers were not able to sufficiently suppress adventitious moisture, they were not even able to measure the –1/0 process. Starting from perchlorate salts of the cations, produced by metathesis of the chlorides produced from the Hertz reaction, these workers found a reversible 0/+1 process, but this was followed by a 6-electron wave producing the orthoaminothiols and -selenols. Re-determination of the benzo derivative **53** using cyclic voltammetry at a stationary platinum electrode has recently been undertaken [78]. Under these conditions, the –1/0 process *could* be measured, but was found to be electrochemically irreversible. There is no experimental evidence for the isolation of an anionic single-ring dithiazole.

If we consider the +1/0 redox couple, which has been measured for all the 1,2,3-dithia- and diselenazoles listed in Table 5, we find the following trends. First, the potentials measured by polarography [76,77] are quite different from those obtained at a stationary Pt electrode [78] (–0.26 vs. +0.18 V). These data cannot therefore be compared with each other. (In a recent review, the potentials measured by polarography for this class of rings have erroneously been assigned positive signs [4]). As mentioned above, given the known tendency of this isomer to cleave a S–S bond, the use of mercury electrodes is not recommended in the first place. Nevertheless, the four compounds measured in the Russian and Czech labs form a nice series in which S and Se were systematically replaced. The results are quite interesting, since they show that replacement of the sulfur at the 2 position in the ring with selenium causes a +0.1 V anodic shift, similar to that observed for the thiadiazoles and the effect *per chalcogen* in the 1,2,3,5-dithiadiazole/selenazole series [28]. However, replacement at the 1 position has no effect on the potentials. Consideration of the coefficients of the redox orbital at the AM1 or PM3 level of theory does not provide an obvious explanation for this difference. A careful re-examination of the electrochemistry of these four compounds seems warranted, in conjunction with a higher-level theoretical study.

To date **58** represents the only non-fused example of a monomer 1,2,3-dithiadiazole to have been characterized electrochemically. This simple five-membered ring has the highest cell potential (E_{cell} = 1.5 V) of the compounds for which both redox processes have been determined in Table 5. By comparison the fused-ring compound **53** has E_{cell} = 1.2 V. As seen previously under our consideration of thiadiazoles, the –N=S=N– group has a powerful electron-withdrawing effect on redox properties of heterocyclic systems. Thus **59** has *dramatically* more anodic values for both processes (e.g. by comparison with **53** or **57**); yet the effect is reasonably even on both processes, so that the measured E_{cell} is still large at 0.99 V. Although this value is still high compared to that of the typical charge transfer salt components, it is sufficient for **59** to be the first genuine example of a neutral radical conductor (NRC). Despite the fact that it adopts a slipped • -dimer stack in the solid state, it has a room temperature conductivity of $1 \bullet 10^{-4}$ S cm^{-1}, which is attributed to an electron hopping mechanism [78].

Insert Fig. 3 here

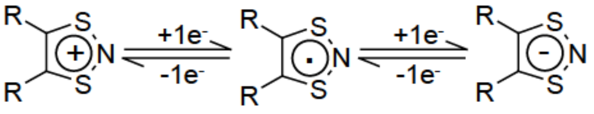
The cyclic voltammograms of **59** and its 2,1,3-isomer **72**, shown in Figure 3, are exceptional compared to other dithiazoles in displaying fully reversible waves at RT for both the 0/+1 *and* the –1/0 processes. Although this *may* reflect genuinely greater chemical stability of all three redox states for these compounds, it should be remembered that electrochemical irreversibility does not always imply chemical instability. Indeed, it is our observation that redox processes in the extremes of low– or high–potentials often appear irreversible. Thus it may be that the *reversibility* of both waves for these two compounds simply reflects the favourable redox potentials for the two redox processes induced by the strongly electron-withdrawing thiadiazolopyrazine "substituent" on the dithiazole rings.

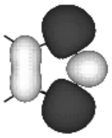
By comparison with their non-fused analogues, the 1,2,3,5-dithiadiazoles, the 1,2,3-dithiazoles show much more dramatic variation in the potential of both redox processes and E_{cell} values, suggesting that with suitable structural variation and substituent effects, more examples of this system may be tuned into functioning NRC's.

We consider now the bifunctional dithiazoles such as **60** - **64**, for which dramatic lowering of the E_{cell} values have been achieved, well within the range of cell potentials observed for TTF and TCNQ. A contributing factor here no doubt is the strongly quinoidal structure of the organic • -systems that are induced by the patterns of substitution represented by these compounds. The lowest E_{cell} value is for **64** at 0.25 V between the +1/+2 and 0/+1 couples. Ironically the coupling of two 7• systems through a *communicative* linkage induces diamagnetic ground states in these systems. (This differs from bifunctional 1,2,3,4-dithiadiazoles, in which there is only very weak communication across bridging backbones, and the ground states effectively consist of isolated doublets.) Thus **60** - **64** have utility in the production of RIC's rather than NRC's. Several of these compounds form conducting salts of their radical cations [79,80]. Note that the radical monoanions are produced at relatively accessible potentials (given the size of these extended ring systems), but to date all these couples have been irreversible, at least at RT. This process bears a more detailed electrochemical investigation. We also note that the +1/+2 couple in **61** is found to be irreversible, which has been attributed to a comproportionation reaction between the neutral form and the di-cation [81]. Such comproportionation reactions are well established for the 1,2,3,5-dithiadiazoles, and may indeed be operative here. Such a reaction should be suppressed if the bulk material in the electrochemical cell were a salt of the mono-cation, and this is another feature that bears further study. We note that the +1/+2 couple in **61** is found at the most anodic potential of the series, so that the absolute energy may also play a role in the irreversibility of this redox process.

4.4 1,3,2-Dithiazoles and 1,3,2-diselenazoles

These are isomers of the 1,2,3- system discussed in section 4.3. Although the synthesis of this class or rings has been extensively explored [82-84], relatively little electrochemical data have been reported. The data tables contain two kinds of compounds, those with and those without substitution on N. The rings in which the Group 15/16 elements bear no substituents are directly comparable to the other compounds in this review, and like their isomers, are 7• -electrons systems in the neutral form [78,85]:





• -SOMO

The redox orbital for the 1,3,2-dithiazole system is unambiguously the • -SOMO indicated above. The absence of a low-lying • -antibonding virtual orbital reflects the much greater strength of C–S and N–S compared to S–S single bonds, which are absent in this isomer.

Although many non-fused 1,3,2-dithiazoles have been reported, only **65** and **66** have been studied by electrochemistry to our knowledge [83]. The data are compiled in Table 6. Monofunctional 1,3,2-dithiazoles are candidates for the construction of NRC's. Bifunctional compounds again face a dichotomy: where there is communication across the carbocylic backbone leading to spin-coupling, they cannot function as NRC's, but may be suitable RIC's; in the absence of coupling the isolated rings may function as NRC’s.

However, when the N atom bears a carbon substituent - the other class of benzodithiazoles listed in Table 6 - the rings are formally saturated, and have an 8• -electron count [86]. A 0/+1 process for these compounds results in the formation of radical cations, and systems of this type might be monofunctional components for RIC's if the potentials are suitable.

To date only a single selenium-containing species has been studied electrochemically [87]. Compound **68** is the diselenium analogue to **67**. The nature of the synthetic route used to produce these dithia- and diselenadiazoles makes the preparation of the mixed S/Se rings considerably more difficult than for the 1,2,3- isomers, for which a direct synthetic route to such mixed systems exists [88]. The data for this compound was obtained under different conditions than the others in the series (see Table 6), and is thus difficult to compare directly. However, for the 1,2,3,5-dithiadiazoles, we have found that the 0/+1 process (that which was measured for **68**) when measured in CH_2Cl_2, is generally 0.2 V more cathodic than when measured in MeCN [14,28]. If this difference applies to the 1,3,2-dithiazoles also, then the potentials for this process in **67** and **68** become indistinguishable. In the case of the 1,2,3-isomer, replacement of S for Se at the position attached to the benzene ring also had no appreciable effect on the redox potential for the 0/+1 process. Our previous experience with dithia- and diselenadiazoles found, however, that the –1/0 process was more affected by Se for S substitution, and that the Se-containing rings had an overall lower E_{cell} than the S-containing analogues [14,28]. There is thus ample warrant for the careful re-investigation of the electrochemistry of compounds such as **67** and **68**, and in particular to try and obtain data for both compounds under the same conditions and measure both the 0/+1 and –1/0 processes. Isolation of the neutral form would be most advantageous for this study to avoid comproportionation. We also draw attention to the huge discrepancy in the values reported for the 0/+1 couple in **65** and **66**. It is at least conceivable that the potentials for **65** at +0.02 and **67** at +0.15 V should differ by this amount between the parent ring and the benzo-fused system. But it is difficult to see that replacement of a single H atom by a methyl group should induce a –0.65 V cathodic shift. These compounds are therefore also candidates for careful re-investigation.

Insert Fig. 4 here

The monofunctional unsubstituted 1,3,2-dithiadiazoles that have been reliably measured indicate a high degree of redox tuning by the substituents [78,85,89]. The cyclic voltammograms of **67**, **69**, **70** and **71** are presented in Figure 4 to highlight graphically the half-volt tunability among these rather similar compounds. If **72**, which contains the previously mentioned thiadiazolopyrazine "substituent", is included, the range of voltages for the 0/+1 process extends over 0.85 V, and that of the –1/0 process over 1.1 V. However, another thing that is immediately obvious from Figure 4 is that E_{cell} - which corresponds to the *separation* between the peaks of the two redox processes - is remarkably constant, being significantly lowered only in the case of **72**. The E_{cell} values for **67**, **69**, **70** and **71** are quite similar to those measured for the 1,2,3,5-

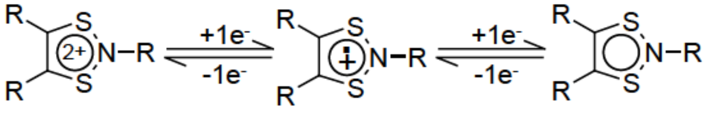
dithiadiazoles (ranges of –1.33 to –1.41 V compared to –1.31 to –1.53 V when measured in acetonitrile solution). We note also that the –1/0 processes for all the compounds in Figure 4 are irreversible at RT, while that of **72** is to date the *only* reported reversible –1/0 process for a mono-functional 1,3,2-dithiazole. These compounds bear further investigation for the dependence of the –1/0 process on scan speed and temperature, and they should also be studied by a.c. voltammetry. We note that, as for the 1,2,3- case, the –1/0 process is reversible precisely when the absolute voltage of the process is brought closer to the centre of the SCE scale (see above).

It is of interest to compare the E_{cell} values for 1,2,3- and 1,3,2- isomers. From the two sets of compounds for which data exits (e.g. **53** vs. **67** and **59** vs. **72**), E_{cell} seem to be slightly smaller for the 1,2,3-'s (by 0.18 V in one case, and 0.07 in the other). This is an issue that clearly bears deeper investigation, although to do so will require considerable synthetic effort to produce the isomers bearing the same substituents.

The only bifunctional 1,3,2-dithiazole that has been studied electrochemically is **73**, originally prepared by Wolmersh user [90] and also by Wudl [91]. As expected for a bifunctional system with strong communication along the carbocyclic backbone, **73** can be reversibly oxidized from the neutral form to the radical monocation and then to the dication [92]. Two irreversible reduction waves were also recorded. The E_{cell} values for the reversible couples in **73** are comparable to those in bifunctional 1,2,3- compounds spaced by a single aromatic ring, but less than the naphtho-bridged **64**.

We consider now the 4*N* annulenes **74** - **78** and see that these do indeed demonstrate reductions to the radical cation and di-cation states (0/+1 and +1/+2 processes in Table 6) [86]. The additional +2/+3 process identified in **77** and **78** probably deals with an oxidation of the substituent aromatic ring, and will not be discussed here. The cell potentials for these compounds are indeed quite small, being approximately –0.5 to –0.3 V, imprecise because the +1/+2 process is in all cases irreversible. The potentials are altogether too anodic to be of use for forming charge transfer salts with conventional acceptors.

Naively one might think that the redox process for **74 - 78**, depicted in the equation below, should be the same as those of the monofunctional 1,3,2-rings with no substituent on N:

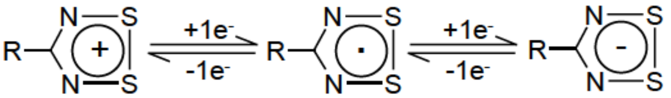


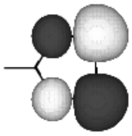
The HOMO when R = H

The redox orbital in this case is the HOMO of the neutral compound, from which one or two electrons are removed in the oxidation processes. Thus the 0/+1 process for these compounds corresponds formally to the –1/0 process for the unsubstituted rings, which is also an 8• /7• couple. However, the redox potentials bear no likeness to one another (e.g. +0.92 V for **74** vs. –1.2 V for **67**). Although, at the AM1 level, the redox orbital bears a formal similarity to that of the unsubstituted dithiazoles (see above), it is not a true • -orbital, because of the pyramidal N atom in the most stable conformation of this anti-aromatic heterocycle (overall C_s symmetry), and it has considerable N-• lone pair character.

4.5 1,2,3,5-Dithiadiazoles and 1,2,3,5-diselenadiazoles

Neutral dithiadiazoles, like dithiazoles, have an odd-electron count and the redox process can be understood as follows:





• -SOMO

The redox orbital for this odd-electron ring system, in the neutral form, is the indicated • -SOMO, from which an electron is either removed in the 0/+1 process, or added in the –1/0 process. This orbital is • anti-bonding with respect to the S–N bond, and *formally* anti-bonding with respect to the S–S bond, but effectively non-bonding because of the long S–S bond distance. It has a node at C.

They are therefore candidates for the construction of NRC's. Calculations and experiment have shown that even bifunctional 1,2,3,5-dithiadiazoles are suitable for this purpose; as a consequence of the nodal pattern of the redox orbital shown above, there is no direct communication of the • -electron system across a carbocyclic backbone, and bifunctional [35] [93] as well as tri-functional 1,2,3,5-dithiadiazoles have been prepared [94,95]. The data in Table 7 include many examples of monofunctional and a few bifunctional examples. Extremely low solubility has prevented the solution electrochemistry of the trifunctional examples from being studied, but there is no reason to assume that they differ from the bifunctional cases in this regard.

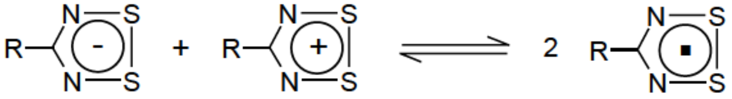
These compounds represent by far the most thoroughly studied redox active Group 15/16 heterocycles by electrochemistry. Both strongly electron withdrawing and electron donating substituents have been studied, with examples where the substituents are directly attached to the five-membered ring (**79 - 86**), and many more where the substituents are remotely attached to a phenyl ring in the *para* position (**87 - 100**), the *meta* position (**101 - 104**) and even in the *ortho* position (**105**), as well as three bifunctional examples (**106 - 108**); in all 30 different heterocycles have been studied. Most have been studied both as salts of the 6• -electron cations and as the 7• -electron radicals (by dissociation of the weakly bound radical dimers in solution). In addition in some cases more than one salt of the same ring system has been studied, e.g. AsF_6^- and PF_6^- salts of **86**. The overwhelming agreement of all this data, obtained by three different research groups, has done much to anchor the reliability of electrochemical measurements of redox active heterocycles and confirm that the experimental approaches are reliable. In particular, the good correspondence in absolute potentials on the SCE scale obtained by both internal referencing using Fc/Fc^+ and external referencing to Ag/Ag^+, both corrected to the SCE scale in separate experiments, is encouraging.

Examples where both the RCN_2S_2 and RCN_2Se_2 rings have been studied with the same R group are also included in the table. No synthetic route has been developed for mixed S/Se compounds, and none are known. The influence of Se has been found to be negligible on the 0/+1 redox process, but averages about 0.2 V on the –1/0 process, with the potentials of the Se compounds being more anodic [14,28]. This results in the E_{cell} values for the RCN_2Se_2 rings being ~0.2 V smaller in magnitude than those of the RCN_2S_2.

Many of these compounds have been studied both in acetonitrile and methylene chloride solutions (using the same Bu_4NPF_6 electrolyte) [14,28]. This has shown that solvent dependence in the electrochemistry of redox-active heterocycles is *process-dependent*. Thus it was found that the –1/0 potentials were identical in acetonitrile and methylene chloride, whereas the 0/+1 process was typically about 0.2 V more anodic in methylene chloride. This resulted in E_{cell} values being approximately 0.2 V *larger in magnitude* for the less polar solvent, a result which has been interpreted as being consistent with the fact that gas-phase cell potentials from computations are indeed *much* larger than the solution phase measurements, but that the less polar solvent should mimic the gas-phase properties more closely than the more polar solvent [14]. This work has also confirmed the utility of acetonitrile (the most common aprotic solvent for electrochemistry) as a solvent to probe disproportionation energies in solution, since it more closely reflects the solid-state environment.

The parallel electrochemistry obtained from the salts of the 6• -electron cations and the 7• -electron radicals is consistent with other evidence that 1,2,3,5-dithia- and diselenadiazole dimers dissociate completely into monomeric radicals in dilute solution. There was absolutely no indication from the solution electrochemistry of the presence of a radical cation dimer in solution for any of the systems studied and reported in Table 6. At higher concentrations, dimerization does occur, especially for the diselenadiazole system, as shown by UV-vis spectroscopy [96].

There was, however, one extremely important consequence of using the neutral radical - i.e. the middle-point of the redox triad - as the chemical source for the electrochemical experiment: this was usually the *only* way to get reversible cyclic voltammograms for both the 0/+1 and the –1/0 redox couples. If a salt of the cation is used as a source of bulk material in the electrochemical cell, the 0/+1 process was always reversible, but the –1/0 process was always irreversible. Banister, et. al. have suggested that this electrochemical irreversibility can be attributed to a rapid comproportionation reaction, i.e. due to the establishment of the following equilibrium [42]:



(3)

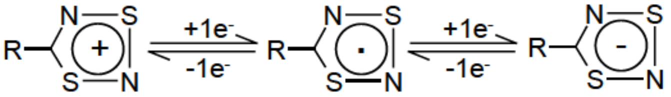
Use of the middle species of a redox triad for the electrochemical experiment prevents this comproportionation reaction. This is an important point when electrochemistry is being used to assess the stability of a triad of redox states. Several examples of irreversible redox processes identified in this review may in fact be due to similar comproportionation reactions, and where it is possible to chemically prepare the middle-species of the triad, that species should be used to measure the electrochemistry of the system. It should be noticed that the kinetics of this comproportionation reaction varies greatly from system to system. In large, non-interacting compounds it is often possible to measure several fully reversible redox processes starting from only a single chemical species. A striking example of this kind of reversibility is found in the *six-stage* reduction of C_{60} by cyclic voltammetry (Figure 5) [97]. But in smaller compounds where the charge reservoir is smaller, several sequential redox steps can rarely be measured from a single starting point.

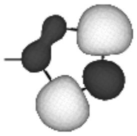
Insert Fig. 5 here

The redox tunability of 1,2,3,5-dithiadiazoles is generally less than the condensed-ring dithiazoles discussed above. Thus for a wide range of remote substituents on the aromatic ring, tunability was on the order of ±0.1 V. No significant difference could be detected from *para* as opposed to *meta* substitution (and in the one case of *ortho* substitution the potentials of the 0/+1 process are identical, cf. **90** vs. **105**). However, this refers to redox tunability *via the carbocyclic •-electron system*. The evidence from compounds **79** to **86** is that a tunability of >0.5 V is obtainable by inductive effects for directly bound substituents. In light of the known electronic/structural effects of R_2N– substituents on thiazyl ring systems, the particularly dramatic effect of a dimethylamino substituent (**84**) warrants further investigation [1].

4.6 1,3,2,4-Dithiadiazoles

The electrochemical data for this isomer of the dithiadiazole ring system is presented in Table 8. The results parallel those of the 1,2,3,5-system in many ways, but there are some important differences as well as similarities. First of all, the redox processes are similar:





• -SOMO

The redox orbital for this odd-electron ring system, in the neutral form, is the indicated • -SOMO, from which an electron is either removed in the 0/+1 process, or added in the –1/0 process.

These systems are thus potentially of interest for the construction of RIC's. They suffer from one major drawback for this purpose which affects the synthetic routes and purification schemes that need to be employed: as the neutral 7• -electron radical, the 1,3,2,4- isomer is unstable both in solution and in the solid state, and isomerizes to the thermodynamically stable 1,2,3,5- isomer [3,98-101]. Indeed, this transformation can be followed in solution by electrochemistry, as demonstrated in Figure 6 [42,102].

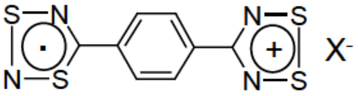
Insert Fig. 6 here.

For this reason, electrochemical data has only been reported starting from salts of the 6• -electron cations. The same problem afflicts this data as observed for the 1,2,3,5- isomers, in that the –1/0 process turns out to be irreversible; perhaps due to a similar comproportionation reaction. Banister, et. al., have also chosen not to report cathodic peak potentials for the irreversible processes, so that we cannot obtain any information on the relative size of E_{cell} for this isomer. From fig. 6 in Ref.[42], it is possible to read a cathodic peak potential for **110** at approximately –1.4 V in acetonitrile solution. If this is indeed accurate, it leads to an E_{cell} of 1.7 V, significantly greater than the 1.43 V measured for the corresponding **86** [14]. The origin of this larger E_{cell} is not well understood, and further speculation is unwarranted until more reliable data is available. It may, for example, be possible to measure the solution electrochemistry of 1,3,2,4- isomers starting from the neutral state in dilute solution at sufficiently low temperature that isomerism is suppressed sufficiently to allow for measurement of the –1/0 processes for a number of examples.

The potentials of the 0/+1 process that have been measured are found to be about 0.27 V more anodic in the 1,2,3,5- isomer. This difference is reflected by semi-empirical MO calculations. Thus analogous AM1 minimized HCN_2S_2 cations have LUMO's (the redox-active orbital for each isomer) at –7.2 and –8.1 eV for the 1,3,2,4- and 1,2,3,5- isomers, respectively. Although it is naïve to assign the absolute redox potentials to gas-phase calculations, it may be that these isomeric systems are sufficiently equally solvated by acetonitrile to make the comparison a valid one.

Insert Fig. 7 here.

Some of the most interesting results have been obtained for the mixed ring bifunctional examples **133** and **134**. Thus the CV shown in Fig. 7 indicates the presence of both redox processes. This is a unique example of a *non-communicating* radical cation. Although the separation between the half-waves in **133** is only 0.29 V, this is not truly a cell potential because the biradical is non-communicating. To date no transport properties have been measured for solid samples of **133**, nor has a crystal structure been reported. It may be that the instability of the biradical in solution precludes the preparation of crystalline sample. We note that the radical cation would indeed have the unpaired electron at the (unstable) 1,3,2,4-ring of the molecule, since the 1,2,3,5-ring has the more anodic potential for the 0/+1 process:

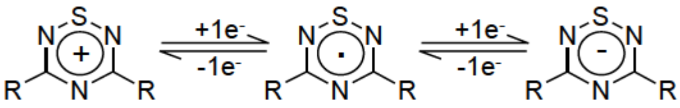


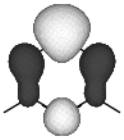
5. Six-membered ring systems

Far less is known about the electrochemical properties of redox-active six-membered heterocycles. Indeed such ring systems have received far less study, and are often less stable and harder to synthesize than the numerous kinds of five-membered ring compounds. Data on thiatriazines and the closely related, fused-ring, dithiadiazines are presented in Table 8, while carbocyclic and heterocyclic dithiatriazines are included in Table 9. There are also metallacyclic dithiatriazines, which have been placed in Table 14 because the redox processes have been shown to be metal-centred rather than ring-centred.

5.1 Thiatriazines

The six-membered thiatriazine ring system is another case where the neutral form is a 7• -electron system, so that mono-functional thiatriazines are candidates for the construction of NRC's [103]. The sole neutral thiatriazine that has been structurally characterized contains a strongly dimerized unit that shows no long range stacking in the solid state. For this reason, the thiatriazines seem to have been bypassed in the search for new NRC candidates. The redox process can be represented as:





The redox orbital in this system is unambiguously the indicated • -SOMO, although the anionic form has only been structurally characterized as a neutral imine derivative, which no longer has • -symmetry [103].

Of the compounds listed in Table 9, only some examples are directly comparable. Compound **135** was measured under protic conditions, and only the –1/0 redox process was measured. Compounds **136**, **137** and **139** are examples of analogous 3,5-diaryl substituted thiatriazines with electron donating and accepting substituents [89]. The S–Cl compounds are not directly comparable, since it is well known that chloride salts of thiazyl compounds have extensive cation-anion interactions; indeed the structurally characterized thiatriazinyl chlorides have covalent S–Cl bonds in the solid state [104].

Two facts are immediately obvious by comparison to the other classes of redox-active heterocycles that have been included in this review. First, the E_{cell} values are fairly high, ranging between about –1.4 and –1.5 V, only slightly smaller in magnitude than the –1.60 V measured (in CH_2Cl_2 solution) for the 1,2,3-5-dithiadiazoles. Second, the redox potentials are tunable to a much larger degree than in the dithiadiazoles. Over a similar range of *para* aryl substituents (from the strongly electron withdrawing NO_2 to the potent donor CH_3O, the range is 0.37 V, whereas for the same range of substituents, the dithiatriazines are tunable by only 0.1 V.

Insert Fig. 8 here

An important difference between the dithiatriazine and all the five-membered thiazyl ring systems discussed above is that the solution electrochemistry clearly evidences the formation of dimers in solution. Consider Fig. 8, which shows the sequential CV's when in a single experiment, progressively more radical-dimer **137** was added to the electrolyte solution using a side-arm addition technique under vacuum. At extremely low concentrations only the two outer waves, each reversible (though distored by the extreme dilution), are observed, but at intermediate concentration there are two peaks of approximately equal height. At higher concentration, the only peaks observed are the inner pair, and the reversibility of the –1/0 process is compromised [89].

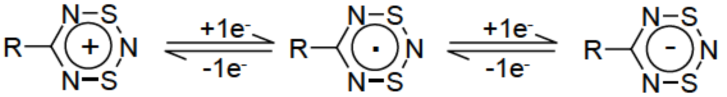
We interpret these results as being due to equilibrium in solution between the radical monomer and the dimer. This has been independently substantiated by quantitative EPR measurement [105]. The identification of the low-concentration limiting voltammogram with that of the monomer in solution was confirmed in a separate experiment in which [3,5-Ph_2-1,2,4,6-$C_2N_3S_2$][PF_6] was used as the starting point for the electrochemistry, i.e. a salt of the 6• -electron cation of **137** [89]. Although the salt does not allow for observation of a reversible –1/0 process (likely due to a comproportionation reaction) the identity of both processes can be confirmed, and the 0/+1 process is in fact identical to that observed in Fig. 8a. The data in Table 9 for **136** and **139** are taken from the outer lines of double-peak data; i.e. the original CV's resembled Fig. 8b.

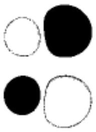
The other noteworthy entry in Table 9 is the P(V) analogue to the organic thiatriazines, **145**. The measured potential (albeit by polarography in acetonitrile solution) for the 0/+1 process in this ring compound is found to be much more cathodic (about 2 volts, a huge difference). It was not clear from ref. [59] exactly which compound was measured in this experiment, and this system bears a careful reinvestigation. We note that the free radical corresponding to the reduction of the cationic compound has been prepared chemically and characterized by EPR spectroscopy [106].

5.2 Dithiatriazines

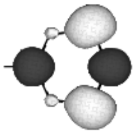
The dithiatriazine ring system is an example of an 8• -electron compound. It is conceivable that it could be oxidized to a 7• -electron radical cation, and hence is conceivable as an RIC component. However, in the one published study on **146** (Table 10), it appears that the 0/+1 process is actually less accessible than the –1/0 process [41]. In retrospect, this may not be too surprising, given the fact that the closely related $S_3N_3^-$, **13**, is a stable compound, and the –1/0 process was measured at +0.17 V for **13** in the same solvent [55]. The extreme insolubility of aryl dithiatriazines is a complicating factor in trying to obtain convincing electrochemical data on this system, and it is clear from NMR data that they dissolve as intact S---S bonded diamagnetic dimers, which will further complicate the electrochemical analysis [107].

The redox processes for this system are shown below:





• -HOMO in C_{2v}



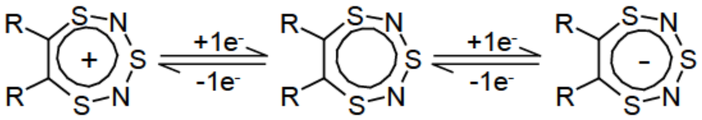
• -LUMO in C_{2v}

Starting from the neutral form, an electron may be removed from the • -HOMO, or added to the • -LUMO. Although it may seem odd to add an additional election to a system that is formally an 8• anti-aromatic heterocycle, it should be noted that the S_3N_3 radical is 9• [108], and the stable $S_3N_3^-$ anion is 10• [56,109].

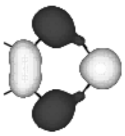
By contrast, the P(V) analogue **147** is extremely soluble, and is monomeric in solution. The S(VI) anion **148** is also an isoelectronic 8• -electron ring system. The sequence of redox potentials for the common –1/0 process for the three ring systems lies in the order E = O_2S^- < PhC < Ph_2P. This is not that expected based on the order of electronegativity. Further analysis of this system should await the re-determination of the electrochemical data under carefully comparable conditions. The insolubility of **146** may be overcome, at least partially, by careful choice of substituent in its derivative chemistry [107].

6. Seven-membered ring systems

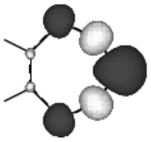
The only seven-membered rings studied electrochemically to our knowledge are two examples of the trithiadiazepine system, for which data is collected in Table 11. This is a 10• -electron ring system, and thus diamagnetic in the neutral state. The redox processes anticipated for this aromatic ring system are:



• -HOMO



• -LUMO

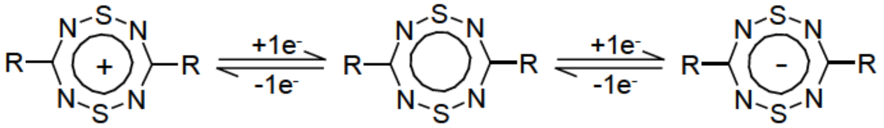


Thus the 0/+1 process involves removal of electrons from the • -HOMO, while the –1/0 process involves addition of electrons to the • -LUMO.

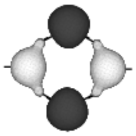
In view of the synthetic routes used to prepare these compounds, several other examples should be capable of being prepared and studied electrochemically. Further analysis of this interesting ring system should await the collection of more data. We note for now that **150** has an extremely high E_{cell}, consistent with its description as a fully aromatic ring system. The drop in E_{cell} in the ring fused analogue **151** is similar to the drop seem between benzene and naphthalene, or naphthalene and anthracene, attributable to a lowering of the HOMO-LUMO gap as conjugation is extended. Indeed, it would appear that the E_{cell} of **151** is similar to that of anthracene. The closest ring systems to compare these compounds to are the 8-membered, 10• -electron dithiatetrazocines to be considered next.

7. Eight-membered ring systems

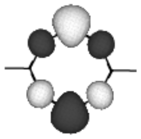
The dithiatetrazocine ring system is an example of a 10• -electron ring system, hence diamagnetic and not particularly of interest in the design of molecular metals. It does, however, present an interesting test case for redox tunability through aromatic carbocyclic substituents. The redox processes, and the two redox-active orbitals involved are depicted below:



• -HOMO



• -LUMO



Again, the 0/+1 process involves removal of electrons from the • -HOMO, while the –1/0 process involves addition of electrons to the • -LUMO.

We now compare the potentials found for the redox processes (Table 12). The –1/0 process is found to vary very little for the substituted aryl derivatives **152 - 157**, being found between –0.9 and –1.0 V for all these species in methylene chloride solution [31]. Starting with the neutral compound this process involves population of the • -LUMO, and the observation of little redox tuning is fully consistent with the presence of nodes at C in this MO.

On the other hand, the potentials for the 0/+1 process vary systematically with the remote substituent, from +1.50 V for the donor substituent CH_3O to +2.00 V for the withdrawing substituent CF_3. Since this process involves removing an electron from the • -HOMO of the molecule, an orbital with a large coefficient at C, it is to be expected that the carbocycle should mediate a large influence of the substituent on the redox potentials. Consisten with one fixed and one varying redox potential, the "E_{cell}" for this ring system (actually a stability window for the neutral form) varies greatly from 2.45 to 2.91 V.

The electrochemical data for the bent ring system **159** are remarkably similar to the planar aromatic ring compounds **152** – **158** [31]. However, it has both the 0/+1 and –1/0 processes shifted to more cathodic values by almost 0.4 V. Compound **159** can be compared with the P(V) analogue **160**, for which the –1/0 couple was measured at –1.37 V by cyclic voltammetry [110]; it would be interesting to measure this compound in methylene chloride to allow direct comparison with **159**. This study also reports chemical evidence for the existence of the di-anion of **160**, observed as an intermediate by the super-hydride reduction of **160**, which goes on to react with metal halides to form complexes formally derived from the dianion. The radical anion of **160** was shown to be unstable in acetonitrile [110]. The chemical resistance to oxidation of **160** is reflected in the electrochemistry by the absence of a facile oxidation process, unlike what is observed for **159**, both electrochemically and chemically [111].

8. Miscellaneous redox-active heterocycles

In Table 13 we have collected some interesting examples of redox-active heterocycles that do not fit the classifications established above. Compound **161** was discovered by accident from the reaction of elemental sulfur with 1-methylimidazole [112]. It is remarkable in showing two reversible reductions despite the presence of an N–H proton on both rings. The relatively small

E_{cell} and the low range of the potentials for the –1/0 and –2/–1 redox couples suggest that this compound is worthy of further investigation for solid-state conductors, where it could act as an electron acceptor. No attempts have been made, to our knowledge, to form CT salts between **161** and, for example, TTF (**3**).

Heterocycles **162** to **164** are relevant to the use of organosulfides as electrolytes for sodium-sulfur electrochemical storage cells [113]. The first two examples - a C_xS_y diketone and dithioketone, respectively - have extremely small E_{cell} values, but to date have not been used for CT salt preparation, where they could also act as potent acceptors just like **161** [112]. The dimercaptothiadiazole **164** has been studied as a possible solid-redox-polymerization electrode for sodium-based storage cells [114]. On oxidation of the di-anion of **164**, it spontaneously polymerizes with the formation of disulfide bonds. On reduction, these bonds are once again broken. The initial oxidation occurs at –0.3 V, and the reduction at –1.1 V. This represents another example of a EI-CR process (see section 4.2 for a definition). The electrochemical experiment can be modified to produce various oligomeric species in solution as well.

The 4*N* anulenes **165** to **173** have been the subject of a careful comparative electrochemical study [115]. These 8• -electron dithiazines are expected to be able to lose electrons to give potentially more stable 7• radical anions and 6• dications, the latter being a Hückel • -system. Indeed, most of these compounds show two 1-electron oxidation steps. The +1/+2 couple, when observed, is always found to be irreversible, which has been attributed to a rapid comproportionation reaction between the small amount of dianion and the bulk neutral species to form two molecules of the radical cation [115]. A similar effect operates for dithiadiazoles (see above) [42]. No attempt was made to chemically prepare the radical cations and use these as the bulk material in the electrochemical cell, which is an effective way to test the comproportionation hypothesis [28]. We note that the E_{cell} values for these compounds are significantly smaller than observed for the five and six-membered rings which start as 6• -electron cations and are then reduced to the neutral radical and the mono-anions. The very anodic values for both redox couples is reminiscent of the data for the 8• -dithiazoles listed in Table 6. In contrast to the anti-aromatic unsaturated compounds, the electrochemistry of the saturated analogue **174** does not show a reversible 0/+1 couple; indeed the CV has all the hallmarks of an electrochemically irreversible, but chemically reversible process. Oxidation of one of the sulfur atoms in this ring may well induce a structural change with the formation of a S–S bond across the ring, or something along those lines [92].

Heterocycles **177** and **178** are interesting examples of a strategy that tries to incorporate both a donor and an acceptor site within a single organic small molecule [116]. They can be thought of as fusions of the donor heterocycles **175** and **176** with the acceptor **179**, which is a TCNQ analogue. Indeed, the electrochemical data for the mixed compounds are indeed oxidized at potentials comparable to those of **175** and **176**, and reduced at potentials (–1/0 process) similar to that of **179**. The chemistry of composite donor-acceptor heterocycles has recently been reviewed [70]. Thianthrene, **180**, is a long-known sulfur-containing aromatic dye. It has been shown that oxidizing this neutral 4*N* anulene to the +1 state causes the molecule to planarize [117]. The estimated E_{cell} for this ring is only about 0.35 V. In summary, heterocycles containing only C and S demonstrate significantly lower E_{cell} values than all the compounds in this review that incorporate both sulfur and nitrogen. However, such compounds often suffer from a tendency to form strong (though reversible) C–C bonded dimers and oligomers, whereas the thiazyl rings form only weakly bound dimers in the solid state which are reversible on dissolving.

9. Metallacycles

We have collected the electrochemical data for metallacycles incorporating several Group 15 and/or Group 16 elements into the single Table 14. The metallacycles differ greatly from the main-group derivatives, as well as from each other. It has been argued that for some, such as **181** - **199**, there is a high degree of metal-ring covalence, while in others such as **210** and **211** the redox chemistry seems to be primarily metal-centred. In fact for all these systems the metals and their *d*-orbital electrons play an extremely important role in the observed electrochemistry.

For example, in **181** and **182**, which are the only examples of numerous S_2N_2 and S_2N_2H complexes that have been studied by electrochemistry, the influence of the Cp and Cp* rings on the redox potentials are extremely similar to that observed in the related metallocenes. Indeed the electron-donating effect of the five methyl groups on the Cp ring of **182** is completely sufficient to explain the 0.35 V more cathodic reduction potential of the latter [32]. We note that these compounds are organometallic analogues to the 1,3,2,4-dithiadiazoles (Table 8). Unlike the carbocyclic analogues, the reduced forms of **181** and **182** do not seem to be susceptible to isomerism to the 1,2,3,5- form. These metallacycles can be compared to **183** and to the nitrogen-containing metallacyclotetrazoles **184** - **188**, and to the metalladithiolenes **189** - **193**. At the time of our investigation of **181** and **182**, there was no well-established series of redox potentials for CpCo dithiolenes to compare our results to. This deficiency has been alleviated by an excellent electrochemical study of a whole series of systematically related dithiolene compounds [118]. Thus the potentials for the –1/0 couples of **181** and **189** are extremely comparable. **182**, **183**, and **193** form an interesting series, and suggest that 'PhC' is a non-innocent substituent on metallacycles of this type. The dithiolene complexes demonstrate the expected trend on substitution of H for R groups depending on whether these are electron withdrawing (**191**, **192**) or electron releasing (**190**).

The bifunctional complexes **194** to **198** provide electrochemical evidence for strong electronic coupling between the rings, thus supporting the idea that the redox processes involve the ring atoms and not just cobalt. The E_{cell} values for these compounds are very small, suggesting that they may be of utility in the design of conducting molecular solids. We note, however, that both redox processes are very cathodic even with Cp rather than Cp* coordinated to the metal; also as radical anions these would have to act as *n*-type rather than the more common *p*-type metals (such as TTF^+).

The electrochemistry of the *ortho*-thiopyridine complexes **200** – **203** seem to be essentially metal-based processes, in which M(IV) is converted to M(V). The cyclic compounds **200** and **202** are almost 1V harder to oxidize than the corresponding thiolato complexes. The authors do not report any calculations that might shed light on the origin of this large change[119].

Complexes **204** - **209** are metallacyclic derivatives of the 1,2,3,5-dithiadiazoles **86**, **94** and **97**. They are of interest in that some are radicals (**207** - **209**), while others have abstracted a proton in order to achieve a diamagnetic "18-electron" configuration. This behaviour reflects the general tendency of, for example, electron-rich organometallic nickel complexes to be stable (especially as clusters), while iron organometallics have a strong tendency to obey the 18-electron rule [33]. We note that the E_{cell} of the nickel cluster **207** is 1.24 V, whereas that for the parent ring compound **86** it is 1.43 V. Although not a dramatic change, it is in the right direction. This encouraging result suggests that organometallic derivatives of free radical Group 15/16 heterocycles deserve further study for the preparation of interesting molecular conductors. Their applicability to molecular magnet design (of which the known examples include many metal complexes) should also be considered [120].

The analogous Pt(II) complexes **208** and **209** seems to have rather disparate E_{cell} values, the former being *smaller* than the nickel complex **207**, the latter considerably larger. These interesting radical metallacycles bear further investigation [121].

The redox potentials of the metalladithiatriazines **210** and **211** have been explained convincingly by a consideration of the degree of metal-nitrogen multiple bonding involved in these rings, by comparison with a number of other molybdenum and tungsten complexes [34]. Whereas a • -electron-rich dithiatriazine group would be expected to be readily oxidized, the metallacycles are not oxidized electrochemically to the limit of the solvent range (CH_2Cl_2). This has been explained as due to strong donation from the $2a_2$ • * orbital (the HOMO for an $N_3S_2^{3-}$ moiety) to an empty metal *d*-orbital in $MoCl_4^{2+}$.

10. Conclusions and further work

The data incorporated into this review falls into two broad classes: those which are the result of careful comparative studies, usually with a series of compounds bearing variable substituents, and those that are taken from single measurements carried out in isolation from other electrochemical studies. We believe that the results demonstrate the critical importance of the former approach. Many Group 15/16 heterocycles are extremely sensitive to hydrolysis, as well as to aerial oxidation for those species that are prepared in the radical form. Therefore studying a series of closely related compounds is *essential* in order to weed out false data caused by performing good electrochemical experiments on poor samples. Throughout the review, we have indicated where, in our judgment, additional experiments or careful re-determination of electrochemical data is warranted. We hope the community of researchers in this field will agree, so that many of the gaps in our current understanding will soon be filled. We sincerely hope that the comprehensive data compiled in this review will serve as useful guideposts for the continued development of Group 15/16 heterocyclic chemistry.

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Tables of electrochemical data

(these follow the figure captions in a separate electronic Section of the document)

Figure Captions

Fig. 1. Two cell designs for operation under vacuum or pressure, which allow the handling of extremely air and moisture sensitive compounds. (a) Design described first in Ref. [40], which uses break-seal techniques. The break-seals can be loaded in a Glove Box, and are fused to the cell prior to rigorous vacuum drying and loading of electrolyte and solvent. (b) Design utilizing swage-lock technology to produce a pressure- and vacuum proof cell. Described in Ref. [39], with improvements to the reference electrode described in Ref. [42].

Fig. 2. Steady-state cyclic voltammogram of **41** in MeCN containing Bu_4NBF_4 (0.2 M), scan rate = 300 mV sec^{-1} (adapted from Ref. [73]). The –1/0 process is electrochemically irreversible but chemically reversible (EI-CR).

Fig. 3. Fully reversible redox couples in the CV occur for both the –1/0 and 0/+1 couples of (a) the 1,2,3-dithiazole **59** and (b) the isomeric 1,3,2-dithiazole **72** (0.1 *M* Bu_4PF_6 in MeCN, scan rate = 100 mV sec^{-1}). The former has a noticeably smaller E_{cell} value. Adapted from Ref [78].

Fig. 4. Comparative CV's of four mono-functional 1,3,2-dithiazoles, showing the high degree of tuning that fused substituents have on the redox potentials. There is much less variation

in the E_{cell} values, however, as both the (irreversible) –1/0 and (reversible) 0/+1 processes are shifted by about the same amount. Adapted from Ref [13].

Fig. 5. In the large, spherical C_{60}, which is not expected to have strong overlap with neighbouring molecules, six reversible reduction steps can be observed in (a) the CV, and (b) the differential pulse voltammogram, starting from the neutral molecule. Adapted from Ref [97].

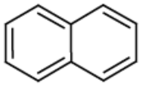
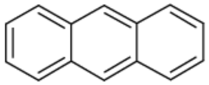
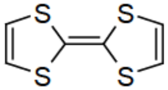
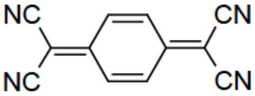
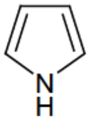
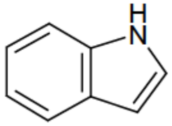
Fig. 6. CV of the 1,3,2,4-dithiadiazole **110** as its AsF_6^- salt recorded at –10°C in MeCN containing 0.1 *M* ^{n}Bu$_4$NBF$_4$. The asterisk marks the onset of peaks due to the isomerized 1,2,3,5-dithiadiazole radical **86**. Adapted from Ref [42].

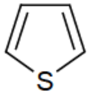
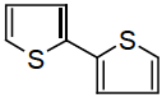
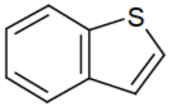
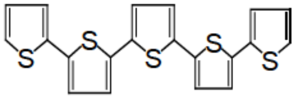
Fig. 7. CV of the mixed-isomer dithiadiazole **133** as its *bis* AsF_6^- salt recorded at –10°C in MeCN containing 0.1 *M* Bu_4BF_4. Adapted from Ref [122].

Fig. 8. Cyclic voltammograms for 3,5-diphenyl-1,2,4,6-thiatriazinyl in CH_2Cl_2 solution (0.1 M Bu_4NPF_6). (a) At extremely low concentration, a (distorted) CV shows the 0/+1 and –1/0 processes for the monomeric radical **137**. (b) At intermediate concentration, an undistorted CV has waves for both the monomeric radical and its dimer. (c) At a higher concentration the CV is dominated by signals due to the dimer [89].

Table 1.

Benchmark electrochemical data

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **1**	–1/0 0/+1	–2.50 +1.54		4.04	P - DME - MeCN - Pr_4NClO_4 - SCE P - RPE - MeCN - Pr_4NClO_4 - SCE	[43]
 **2**	–1/0 0/+1	–2.00 +0.73	R at RT	2.73	CV - Pt - DMF - Bu_4NClO_4 – SCE CV – Pt – CH_2Cl_2 – Bu_4NBF_4 - SCE	[44]
 **3**	0/+1 +1/+2	+0.33 +0.70	R at RT	0.37	CV - Pt - MeCN - [f] - SCE	[17]
	0/+1 +1/+2	+0.37 +0.67	R at RT	0.30	CV - GC - CH_2Cl_2 - Bu_4NClO_4 - SCE	[45]
 **4**	–2/–1 –1/0	–0.37 +0.18	R at RT	0.55	CV - Pt - MeCN - Bu_4NBF_4 - SCE [g]	[18]
 **5**	0/+1	1.2 p_a	IR due to polymerization		CV - Pt - MeCN - Bu_4NPF_6 - SCE	[123,124]
	0/+1	1.26 p_a	IR due to polymerization		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[125]

6						
 **7**	0/+1	2.06 p_a	IR due to polymerization		CV - Pt - MeCN - TEAP - Ag/Ag^+	[126,127]
 **8**	0/+1	1.32 p_a	IR due to polymerization		P - DME - MeCN - Et_4NClO_4 - Ag/Ag^+	[126,127]
 **9**	0/+1	1.75 p_a	IR due to polymerization		CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[125]
 **10**	0/+1 +1/+2	+0.820 +1.120	R at RT R at RT	0.30	CV - GC - CH_2Cl_2 - Et_4NBF_4 - SCE [h]	[128]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

[d] • E_{cell}• = • $E_{ox} – E_{red}$• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

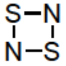
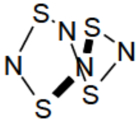
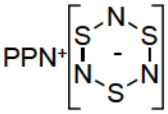
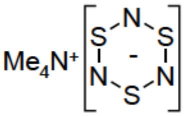
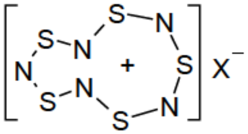
[f] Electrolyte not specified.

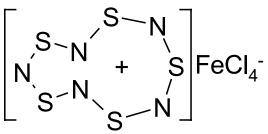
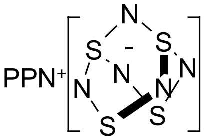
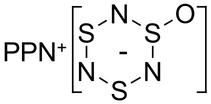
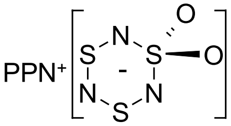
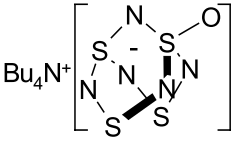
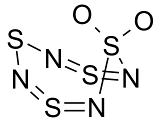
[g] Ag/AgCl used, converted to SCE scale.

[h] SCE calibrated against external Fc/Fc^+ using +0.408 vs. SCE as the conversion factor.

Table 2.

Electrochemical data for binary Group15/16 compounds

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **11**	–1/0 0/+1	–0.85 +0.1	*ca.* 10^{-3} *M* at 16.5°C	0.95	CV - Pt- MeCN - Bu_4NBF_4 – SCE [f]	[57]
 **12**	–1/0	–0.43	QR at –25°C; IR at RT		CV - Pt - MeCN - TEAP - Ag/Ag^+	[58]
	–1/–2 –1/0	–2.14 –0.94	Wave incr. at low T. Pre-wave at –0.65 V.		P - DME - MeCN - Et_4NClO_4 - Ag/Ag^+	[54]
 **13**	–1/0	+0.17	R at RT (E_a–E_p) = 0.08V		CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[55]
	–1/–3	–2.455	product unstable		P - DME - MeCN - Et_4NClO_4 - Ag/Ag^+	[54]
 **14**	0/+1 0/+1	+0.19 +0.06	X = BF_4^- QR at –18.5°C X = AsF_6^-		CV - Pt - MeCN - Bu_4NBF_4 – SCE [f] CV - Pt - MeCN - Bu_4NBF_4 – SCE [f]	[39] [129]

	0/+1	+0.46	IR at all T	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[60]
 **15**	–3/–1 –1/0 0/+1	–2.105 –0.12	IR (also studied at RPE). IR - product unstable. Oxidation produces S_5N_6	P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[54]
 **16**	–3/–1	–1.53	IR	P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[62]
 **17**	–3/–1 –1/0	–1.63 –0.06	R (also studied on RPE and by CV)	P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[62]
 **18**	–3/–1	–1.91	R (also studied on RPE and by CV)	P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[62]
 **19**	reaction	–0.28	IR	P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[62]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

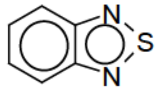
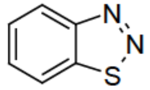
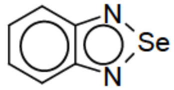
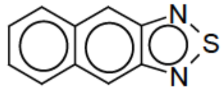
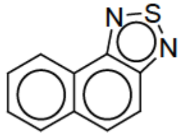
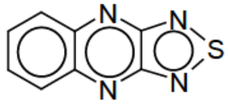
[d] • E_{cell}• = • $E_{ox} – E_{red}$• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

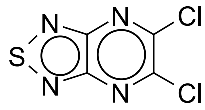
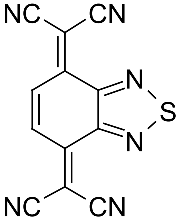
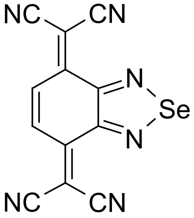
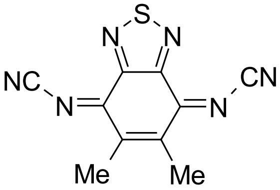
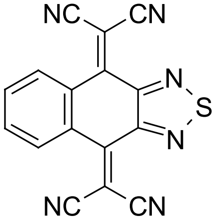
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

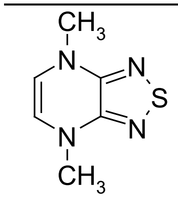
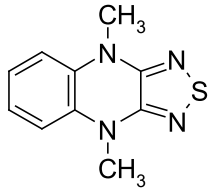
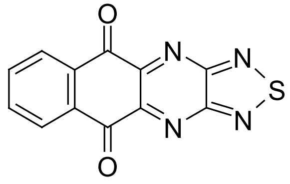
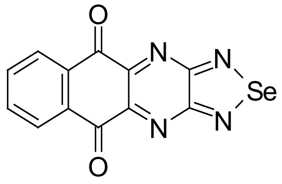
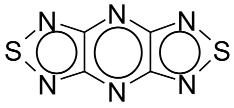
[f] Ag/Ag^+ reference electrode calibrated to the SCE scale.

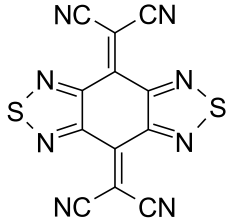
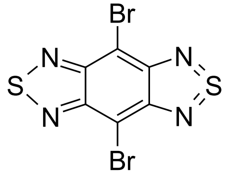
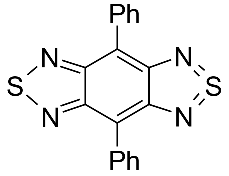
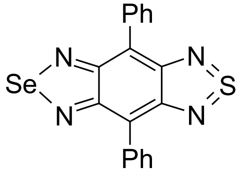
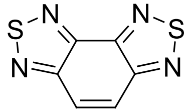
Table 3.

Electrochemical data for Thiadiazoles and Selenadiazoles

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **20**	2/–1 –1/0 0/+1	–2.5 –1.51 +2.2	IR at RT R at RT	0.99	CV - Hg - MeCN - Bu_4NClO_4 – SCE[f] P - RPE - MeCN - Et_4NClO_4 - SCE	[130]
 **21**	–1/0	–1.64			CV - Hg - MeCN - Bu_4NClO_4 - SCE[f]	[130]
 **22**	–2/–1 –1/0	–2.3 –1.38	IR at RT R at RT	0.92	CV - Hg - MeCN - Bu_4NClO_4 - SCE[f]	[130]
 **23**	–2/–1 –1/0	–1.9 –1.16	IR at RT R at RT	0.74	CV - HG - MeCN - Bu_4NClO_4 - SCE[f]	[130]
 **24**	–2/–1 –1/0	–2.5 –1.64	IR at RT R at RT	0.86	CV - Pt - MeCN - Bu_4NClO_4 - SCE[f]	[130]
 **25**	–1/0	–0.46	RT		CV - Pt - MeCN - Et_4NClO_4 - SCE	[131]

 **26**	–1/0	–0.56	RT		CV - Pt - MeCN - Et_4NClO_4 - SCE	[131]
 **27**	–2/–1 –1/0	–0.38 +0.12	RT RT	0.30	CV - Pt - MeCN - Et_4NClO_4 - SCE	[20]
 **28**	–1/0	+0.04	RT		CV - Pt - MeCN - Et_4NClO_4 - SCE	[67]
 **29**	–2/–1 –1/0	–0.55 –0.01	RT RT	0.56	CV - Pt - MeCN - Et_4NClO_4 - SCE	[20]
 **30**	–2/–1 –1/0	–0.38 –0.21	RT	0.17	CV - Pt - MeCN - Et_4NClO_4 - SCE	[68]

 **31**	0/+1 +1/+2	+0.15 +0.95	R at RT IR at RT	0.80	CV - Pt - MeCN - $\mathrm{Et_4NClO_4}$ - SCE	[67]
 **32**	0/+1 +1/+2	+0.54 +1.30	R at RT IR at RT	0.76	CV - Pt - MeCN - $\mathrm{Et_4NClO_4}$ - SCE	[67]
 **33**	–3/–2 –2/–1 –1/0	–1.44 –1.18 –0.25	Chemically reversible electrolysis	0.93	El - Pt - MeCN - $\mathrm{Bu_4NClO_4}$ - SCE	[69]
 **34**	–3/–2 –2/–1 –1/0	–1.35 –1.03 –0.20	Chemically reversible electrolysis	0.83	El - Pt - MeCN - $\mathrm{Bu_4NClO_4}$ - SCE	[69]
 **35**	–2/–1 –1/0	–0.82 +0.10	RT RT	0.92	CV - Pt - MeCN - $\mathrm{Et_4NClO_4}$ - SCE	[131]

 **36**	–2/–1 –1/0	–0.49 –0.02	RT RT	0.39	CV - Pt - MeCN - Et_4NClO_4 - SCE	[20,68]
 **37**	–2/–1 –1/0	–1.10 –0.35	R at RT R at RT	0.75	CV - Pt - CH_2Cl_2- Bu_4NClO_4 - SCE	[132]
 **38**	–2/–1 –1/0	–1.30 –0.61	R at RT R at RT	0.69	CV - Pt - CH_2Cl_2- Bu_4NClO_4 - SCE	[132]
 **39**	–2/–1 –1/0	–1.21 –0.53	R at RT R at RT	0.68	CV - Pt - CH_2Cl_2- Bu_4NClO_4 - SCE	[132]
 **40**	–1/0	–1.45	R at RT		CV - Pt - CH_2Cl_2- Bu_4NClO_4 - SCE	[132]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

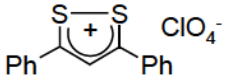
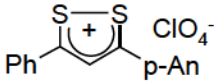
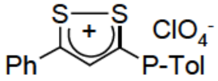
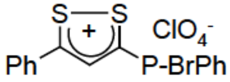
[d] • E_{cell}• = • $E_{ox} – E_{red}$• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

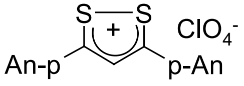
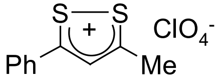
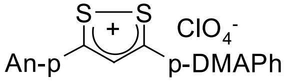
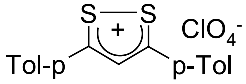
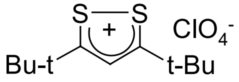
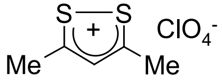
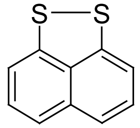
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry, EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

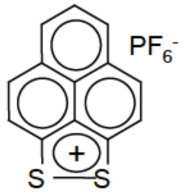
[f] Also determined by ACV at a stationary Hg drop.

Table 4.

Electrochemical data for Dithiole Rings

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **41**	–1/0	–1.14 p_c	IR at RT	0.97	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	0/+1	–0.135	R at RT			
	–2/–1	–1.70	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73,133]
	–1/0	–1.07/–0.35 p_a/p_c	IR but chemically rev	0.80		
	0/+1	–0.235	R at RT			
 **42**	–1/0	–0.96 p_c	IR at RT	0.72	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	0/+1	–0.205	R at RT			
	–2/–1	–1.68	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73]
	–1/0	–1.15/–0.42 p_a/p_c	IR but chemically rev	0.83		
	0/+1	–0.29	R at RT			
 **43**	–1/0	–1.25 p_c	IR at RT	1.05	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	0/+1	–0.165	R at RT			
	–2/–1	–1.68	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73]
	–1/0	–1.19/–0.40 p_a/p_c	IR but chemically rev	0.89		
	0/+1	–0.26	R at RT			
 **44**	–1/0	–1.10 p_c	IR at RT	0.97	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	0/+1	–0.10	R at RT			
	–2/–1	–1.51	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73]
	–1/0	–0.94/–0.30 p_a/p_c	IR but chemically rev	0.75		
	0/+1	–0.16	R at RT			

 **45**	–1/0 0/+1	$-1.01\ p_c$ –0.265	IR at RT R at RT	0.71	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	–2/–1 –1/0 0/+1	–1.69 $-1.27/-0.45\ p_a/p_c$ –0.35	R at RT IR but chemically rev R at RT	0.89	CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73]
 **46**	0/+1	$-0.26\ p_c$	IR at RT; dimerizes on reduction		CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
 **47**	–1/0 0/+1	$-1.04\ p_c$ –0.42	IR at RT R at RT	0.58	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
 **48**	–1/0 0/+1	$-1.28\ p_c$ –0.20	IR at RT R at RT	1.05	CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
 **49**	0/+1	–0.575	R at RT		CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
	0/+1	–0.61	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - SCE	[73]
 **50**	0/+1	$-0.53\ p_c$	IR at RT		CV - Pt - CH_2Cl_2 - Bu_4NBF_4 - SCE	[73]
 **51**	–2/–1 –1/0 0/+1	–2.65 –0.98 +0.95	 R at RT R at RT	1.93	P - DME - MeCN - Pr_4NClO_4 – SCE^f	[43]

 **52**	–2/–1 –1/0 0/+1	–1.55 –0.77 –0.22	QR at RT R at RT R at RT	 0.55 	CV - Pt - MeCN - Bu_4NBF_4 - SCE [g]	[75]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

[d] • E_{cell}• = • $E_{ox} – E_{red}$• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

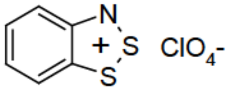
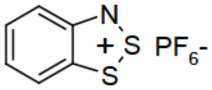
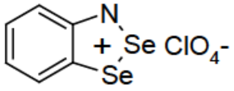
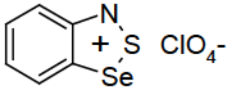
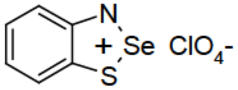
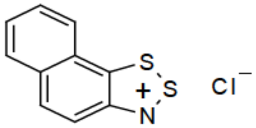
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

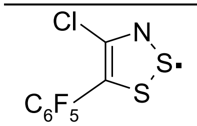
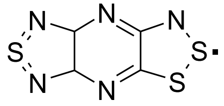
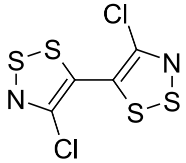
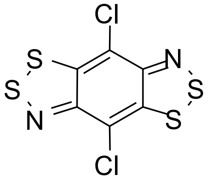
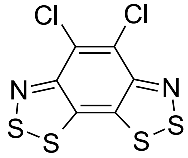
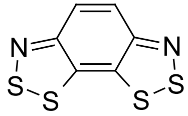
[f] reduction was verified by Cyclic Voltammetry

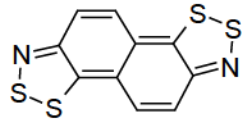
[g] Ag/AgCl used, converted to SCE scale with –0.02 V correction

Table 5.

Electrochemical data for 1,2,3-Dithiazoles and Selenium-containing analogues

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **53**	–6/0 0/+1	–2.22 –0.26	IR at RT R at RT		P - DME - MeCN - Et_4NClO_4 - SCE CV - Pt - MeCN - Et_4NClO_4 – SCE EPR detection of radical	[76,77]
	–1/0 0/+1	–1.0 +0.18	IR at RT R at RT	1.15	CV - Pt - MeCN - Bu_4NPF_6 – SCE[f]	[78]
 **54**	–6/0 0/+1	–2.11 –0.15	IR at RT R at RT		P - DME - MeCN - Et_4NClO_4 - SCE CV - Pt - MeCN - Et_4NClO_4 - SCE	[76, 77]
 **55**	–6/0 0/+1	–2.20 –0.25	IR at RT R at RT		P - DME - MeCN - Et_4NClO_4 - SCE CV - Pt - MeCN - Et_4NClO_4 - SCE	[76, 77]
 **56**	–6/0 0/+1	–2.10 –0.15	IR at RT R at RT		P - DME - MeCN - Et_4NClO_4 - SCE CV - Pt - MeCN - Et_4NClO_4 - SCE	[76, 77]
 **57**	0/+1	+0.40 3	R at RT, scan rate 33 mV s^{-1}		CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - SCE	[73,134]

 **58**	–1/0 0/+1	–1.1 +0.38	IR at RT R at RT	1.5	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[135]
 **59**	–1/0 0/+1	+0.15 +1.14	R at RT R at RT	0.99	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[78]
 **60**	–1/0 0/+1 +1/+2	–1.11 +0.80 +1.25	IR R at RT R at RT	0.45	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[136]
 **61**	–1/0 0/+1 +1/+2	–0.95 +0.93 +1.5	IR at RT R at RT IR	0.57	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[81]
 **62**	–1/0 0/+1 +1/+2	–0.96 +0.81 +1.37	IR R at RT R at RT	0.56	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[79]
 **63**	–1/0 0/+1 +1/+2	–0.98 +0.61 +1.10	IR R at RT R at RT	0.49	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[79]

 **64**	–1/0	–1.06	IR		CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[80]
	0/+1	+0.41	R at RT	0.25		
	+1/+2	+0.66	R at RT			

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

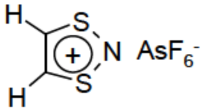
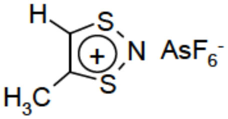
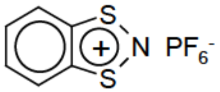
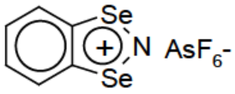
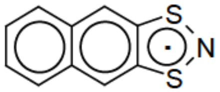
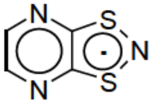
[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

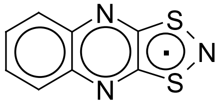
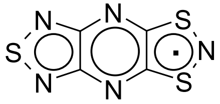
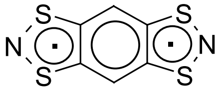
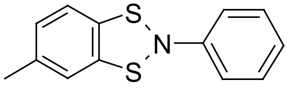
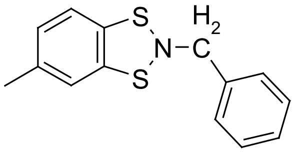
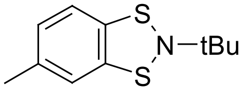
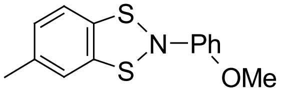
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

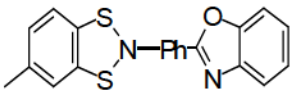
[f] Internal Fc/Fc^+ pseudo-reference electrode converted to SCE scale using +0.38 as the conversion factor in MeCN.

Table 6.

Electrochemical data for 1,3,2-Dithiazoles and selenium-containing analogues

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **65**	0/+1	+0.02	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - Ag/Ag^+	[83]
 **66**	0/+1	–0.63	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - Ag/Ag^+	[83]
 **67**	–1/0 0/+1	–1.2 +0.15	IR at RT R at RT	1.33	CV - Pt - MeCN - Bu_4NPF_6 – SCE[f]	[78,92]
 **68**	0/+1	–0.10	Quasi-reversible (radical unstable at RT)		CV - GC - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[87]
 **69**	–1/0 0/+1	–1.08 +0.27	Strongly IR at RT R at RT	1.35	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[85]
 **70**	–1/0 0/+1	–0.88 +0.53	IR at RT R at RT	1.41	CV - Pt - MeCN - Bu_4NPF_6 - SCE	[13]

 **71**	–1/0 0/+1	–0.73 +0.62	Strongly IR at RT R at RT	1.35	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[85]
 **72**	–1/0 0/+1	–0.06 +1.00	R at RT R at RT	1.06	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[85]
 **73**	–2/–1 –1/0 0/+1 +1/+2	–1.8 –1.3 +0.16 +0.74	IR at RT IR at RT R at RT R at RT	0.5 1.46 0.58	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[92]
 **74**	0/+1 +1/+2 +2/+3	+0.92 +1.39 +2.18	R at RT IR at RT IR at RT	0.47 0.79	CV - Hg - CH_2Cl_2 - Bu_4NBF_4 - SCE[f]	[86]
 **75**	0/+1 +1/+2	+0.93 +1.27	R at RT IR at RT	0.34	CV - Hg - CH_2Cl_2 - Bu_4NBF_4 - SCE	[86]
 **76**	0/+1 +1/+2	+0.72 +1.05	R at RT IR at RT	0.33	CV - Hg - CH_2Cl_2 - Bu_4NBF_4 - SCE	[86]
 **77**	0/+1 +1/+2 +2/+3	+0.86 +1.39 +1.89	R at RT IR at RT IR at RT	0.53	CV - Hg - CH_2Cl_2 - Bu_4NBF_4 - SCE	[86]

 **78**	–1/0?	–1.55	IR at RT		CV - Hg - CH_2Cl_2 - Bu_4NBF_4 - SCE	[86]
	0/+1	+0.90	R at RT	0.41		
	+1/+2	+1.31	IR at RT			
	+2/+3	+1.52	IR at RT			

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[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

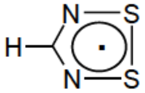
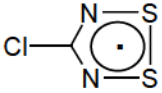
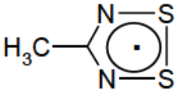
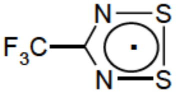
[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

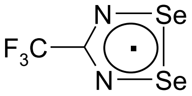
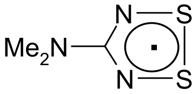
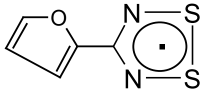
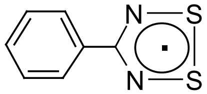
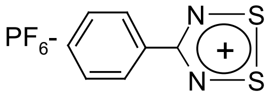
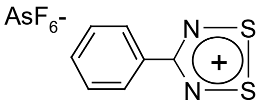
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

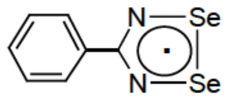
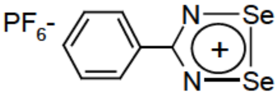
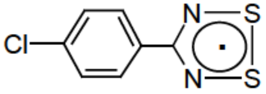
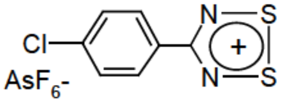
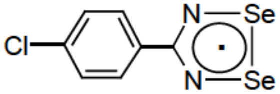
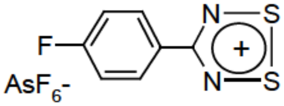
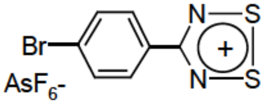
[f] Internal Fc/Fc^+ with pseudo-reference electrode converted to SCE scale using +0.38 as the conversion factor in MeCN.

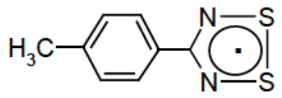
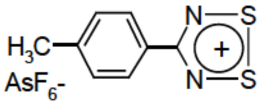
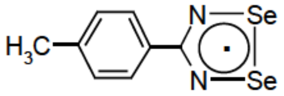
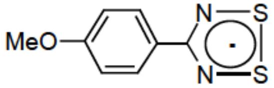
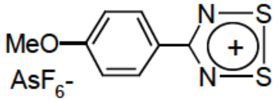
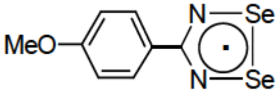
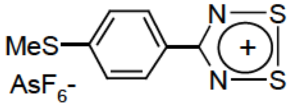
Table 7.

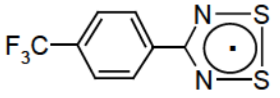
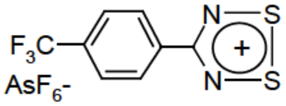
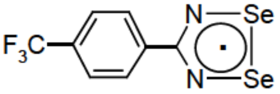
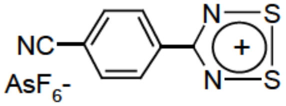
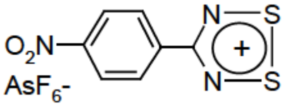
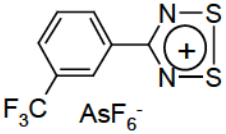
Electrochemical data for 1,2,3,5-Dithiadiazoles

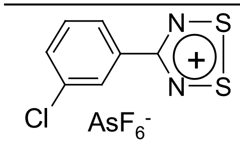
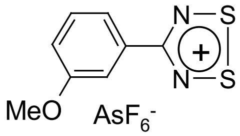
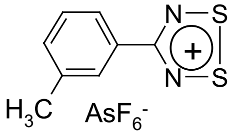
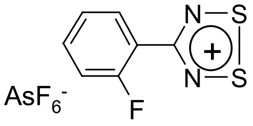
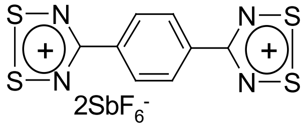
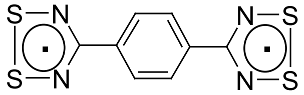
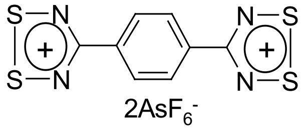
Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
	–1/0	–0.83	R at RT	1.48	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[14]
	0/+1	+0.65	R at RT			
79	–1/0	–0.81	QR, 250mV, • = 200mVs^{-1} at RT	1.67	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[14]
	0/+1	+0.86	R at RT			
	–1/0	–0.63	IR at RT, • = 10 Vs^{-1}	1.46	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[14]
	0/+1	+0.83	R at RT			
80	–1/0	–0.64	IR at RT	1.68	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[14]
	0/+1	+1.04	R at RT			
	–1/0	–0.94	R at RT	1.53	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[14]
	0/+1	+0.59	R at RT			
81	–1/0	–0.88	R at RT	1.66	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[14]
	0/+1	+0.78	R at RT			
	–1/0	–0.42	IR, p_c at • = 200 mV s^{-1} and -20°C	1.33	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[14]
	0/+1	+0.91	R at RT			
82	–1/0	–0.48	R at • = 500mVs^{-1}, RT	1.59	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[14]

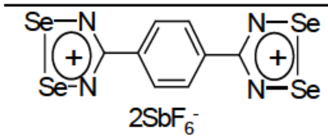
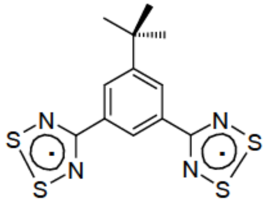
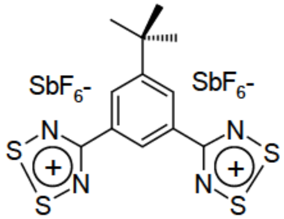
	0/+1	+1.11	R at RT			
	–1/0	–0.41	R at RT	1.30	CV - Pt - MeCN - Bu_4NPF_6 - SCE^f	[14]
	0/+1	+0.89	R at RT			
83	–1/0	–0.39	R at RT	1.49	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{g}	[14]
	0/+1	+1.11	R at RT			
	–1/0	–0.96	R at RT	1.31	CV - Pt - MeCN - Bu_4NPF_6 - SCE^f	[14]
	0/+1	+0.35	R at RT			
84	–1/0	–0.95	QR at RT	1.45	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{g}	[14]
	0/+1	+0.50	R at RT			
	–1/0	–0.79	R at RT	1.42	CV - Pt - MeCN - Bu_4NPF_6 - SCE ^{f}	[14]
	0/+1	+0.63	R at RT			
85	–1/0	–0.81	QR at RT	1.65	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{g}	[14]
	0/+1	+0.84	R at RT			
	–1/0	–0.83	R at RT	1.43	CV - Pt - MeCN - Bu_4NPF_6 - SCE ^{f}	[28]
	0/+1	+0.60	R at RT			
86	–1/0	–0.82	R at RT	1.60	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{g}	[28]
	0/+1	+0.78	R at RT			
	0/+1	+0.68	R at RT		CV - Pt - MeCN - Bu_4NPF_6 - Ag/AgCl	[137]
	0/+1	+0.59	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE ^{h}	[26,42]

	–1/0	–0.61	QR, p_c–p_a = 110mV at • = 200 mV s^{-1} and –10°C	1.24	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
	0/+1	+0.63	R at RT			
87	–1/0	–0.59	R at RT	1.38	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g]	[28]
	0/+1	+0.79	R at RT			
	0/+1	+0.61	R at RT		CV - Pt - MeCN - Bu_4NPF_6 - Ag/AgCl	[137]
	–1/0	–0.81	R at RT	1.43	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
	0/+1	+0.62	R at RT			
88	–1/0	–0.78	R at RT	1.60	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g]	[28]
	0/+1	+0.82	R at RT			
	0/+1	+0.620	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE[h]	[42]
	–1/0	–0.59	QR, p_c–p_a = 100mV at • = 200 mV s^{-1} and –10°C	1.23	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
	0/+1	+0.64	R at RT			
89	–1/0	–0.55	R at RT	1.37	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g]	[28]
	0/+1	+0.82	R at RT			
 **90**	0/+1	+0.600	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE[h]	[42]
 **91**	0/+1	+0.625	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE[h]	[42]

	–1/0 0/+1	–0.89 +0.59	R at RT R at RT	1.48	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
92	–1/0 0/+1	–0.83 +0.77	R at RT	1.60	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[28]
	0/+1	+0.580	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE [h]	[42]
	–1/0 0/+1	–0.61 +0.62	QR, p_c–p_a = 100mV at • = 100 mV s^{-1} and RT R at RT	1.23	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
93	–1/0 0/+1	–0.57 +0.77	R at RT R at RT	1.34	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[28]
	–1/0 0/+1	–0.87 +0.57	R at RT R at RT	1.44	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
94	–1/0 0/+1	–0.85 +0.73	R at RT R at RT	1.58	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[28]
	0/+1	+0.570	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE [h]	[42]
	–1/0 0/+1	–0.68 +0.57	QR, p_c–p_a = 120mV at • 5000 mV s^{-1} and –10°C R at RT	1.25	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
95	–1/0 0/+1	–0.61 +0.74	R at RT R at RT	1.35	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[28]
	0/+1	+0.590	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE [h]	[42]

96						
	–1/0	–0.80	IR at • = 50 – 5000 mV s^{-1} and T = +25 to –0°C	1.46	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
	0/+1	+0.66	R at RT			
97	–1/0	–0.73	IR at • = 50 – 5000 mV s^{-1} and T = +25 to –0°C	1.59	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g]	[28]
	0/+1	+0.86	R at RT			
	0/+1	+0.650	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE[h]	[42]
	–1/0	–0.57	IR at v = 100 mV s^{-1} RT. Return wave at v = 5000 mV s^{-1} and –30°C	1.24	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[28]
	0/+1	+0.67	R at RT			
98	–1/0	–0.53	R at RT	1.39	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g]	[28]
	0/+1	+0.86	R at RT			
 **99**	0/+1	+0.660	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE[h]	[42]
 **100**	0/+1	+0.675	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE[h]	[42]
 **101**	0/+1	+0.645	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE[h]	[26]

 **102**	0/+1	+0.633	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [h]	[26]
 **103**	0/+1	+0.600	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [h]	[26]
 **104**	0/+1	+0.590	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [h]	[26]
 **105**	0/+1	+0.610	QR at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE [h]	[26]
 **106**	–2/0 0/+2	–0.80 +0.61	R at RT R at RT	1.41	CV - Pt - MeCN - Bu_4NPF_6 - SCE [f]	[14,35, 137]
	–2/0 0/+2	–0.72 +0.78	R at RT R at RT	1.50	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [g]	[14,35, 137]
	0/+2	+0.650	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 – SCE [h]	[42]

 **107**	–2/0 0/+2	–0.63 +0.75	R at RT R at RT	1.38	CV - Pt - MeCN - Bu_4NPF_6 - SCE[f]	[14]
 **108**	–2/0 0/+2	–0.79 +0.81	R at RT R at RT	1.60	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g] ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE[g]	[35]
	0/+2	+0.61	R at RT		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[g] ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE[g]	[35]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

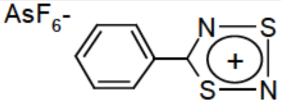
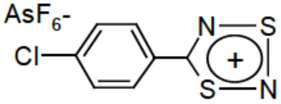
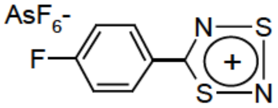
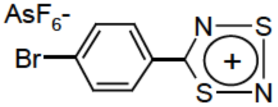
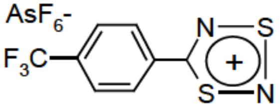
[f] Internal Fc/Fc$^+$ with pseudo-reference electrode converted to SCE scale using +0.38 as the conversion factor in MeCN.

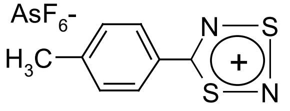
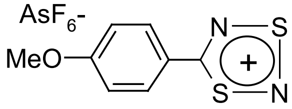
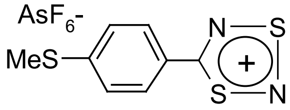
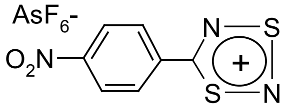
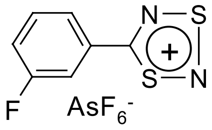
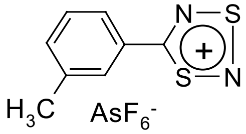
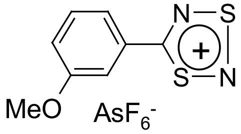
[g] Internal Fc/Fc$^+$ with pseudo-reference electrode converted to SCE scale using +0.48 as the conversion factor in CH_2Cl_2.

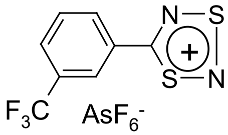
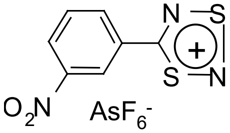
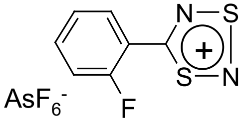
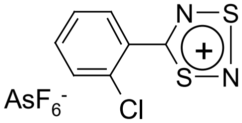
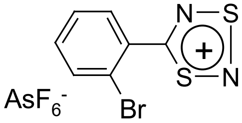
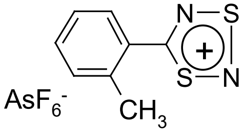
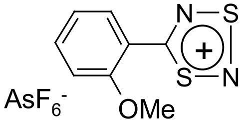
[h] Ag/Ag$^+$ reference electrode calibrated to the SCE scale.

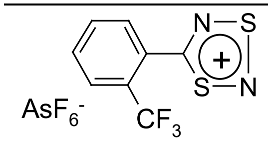
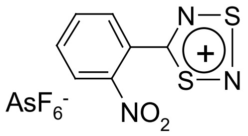
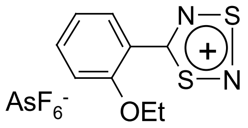
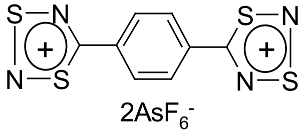
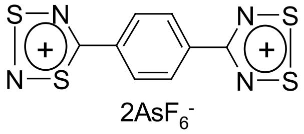
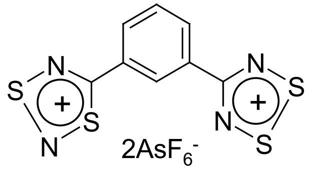
Table 8.

Electrochemical data for 1,3,2,4-Dithiadiazoles

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **109**	0/+1	–0.26	R at RT		CV - Pt - MeCN - Bu_4NBF_4 - Ag/Ag$^+$	[83]
 **110**	0/+1	+0.330	R at –10°C or QR at –10°C ?		CV - Pt - MeCN - Bu_4NBF_4 – SCE [f]	[42,26]
 **111**	0/+1	+0.350	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [f]	[42]
 **112**	0/+1	+0.340	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [f]	[42]
 **113**	0/+1	+0.350	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [f]	[42]
 **114**	0/+1	+0.380	R at –10°C		CV - Pt - MeCN - Bu_4NBF_4 - SCE [f]	[42]

 **115**	0/+1	+0.300	R at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[42]
 **116**	0/+1	+0.290	R at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[42]
 **117**	0/+1	+0.310	R at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[42]
 **118**	0/+1	+0.400	R at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[42]
 **119**	0/+1	+0.370	QR at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **120**	0/+1	+0.320	QR at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **121**	0/+1	+0.330	QR at –10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]

 **122**	0/+1	+0.390	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **123**	0/+1	+0.400	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **124**	0/+1	+0.310	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **125**	0/+1	+0.320	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **126**	0/+1	+0.325	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **127**	0/+1	+0.158	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **128**	0/+1	+0.330	QR at -10^{o}C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]

 **129**	0/+1	+0.403	QR at –10°C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **130**	0/+1	+0.390	QR at –10°C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **131**	0/+1	+0.163	QR at –10°C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[26]
 **132**	0/+2	+0.224	R at –20°C	CV - Pt - MeCN - Bu$_4$NAsF$_6$ - SCE^f	[138]
 **133**	0/+1 +1/+2	+0.303 +0.595	R at –10°C R at –10°C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[122]
 **134**	0/+1 +1/+2	+0.387 +0.647	R at –10°C R at –10°C	CV - Pt - MeCN - Bu$_4$NBF$_4$ - SCE^f	[102]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

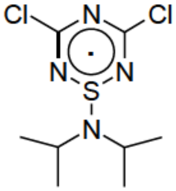
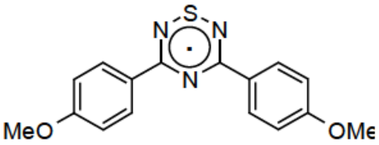
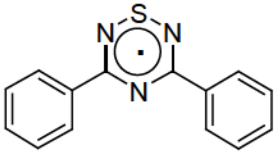
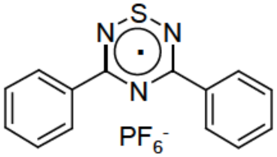
[d] $\bullet E_{cell}\bullet = \bullet E_{ox} - E_{red}\bullet$; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

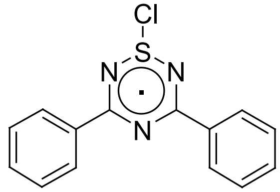
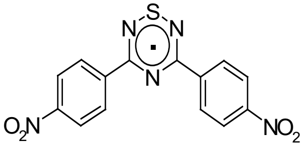
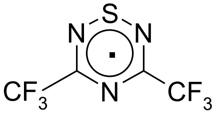
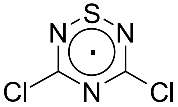
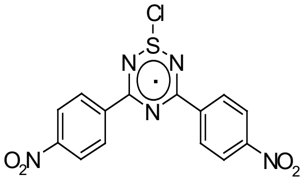
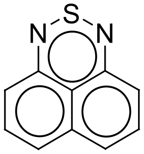
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

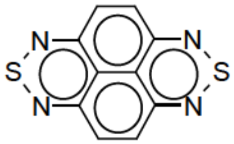
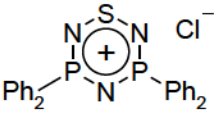
[f] Ag/Ag^+ reference electrode calibrated to the SCE scale.

Table 9.

Electrochemical data for Thiatriazines and Thiadiazines

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **135**	–1/0 –1/0	–1.00 –0.86	pH 2.23 pH 1.87		P - DME - 9MeOH:H_2O - $NaClO_4$ - SHE	[139]
 **136**	–1/0 0/+1	–0.56 +0.76	RT RT	1.32	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE [f]	[89]
 **137**	–1/0 0/+1	–0.46 +0.97	RT RT	1.43	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE [f]	[89]
	–1/0 0/+1	–0.46 +0.97	RT RT	1.43	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE [f]	[89]

 **138**	–1/0 0/+1	–0.48 +0.87	RT RT	1.8	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE^f	[89]
 **139**	–1/0 0/+1	–0.32 +1.13	RT RT	1.45	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	[89]
 **140**	–1/0 0/+1	–0.16 +1.35	RT RT	1.51	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	[89]
 **141**	0/+1	+1.15	RT		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	[89]
 **142**	–1/0 0/+1	–0.32 +1.08	RT RT	1.4	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	[89]
 **143**	–2/–1 –1/0 0/+1	–1.8 –0.96 +1.0	IR at RT R at RT	 1.96	CV - Pt - MeCN - Bu_4NClO_4 - SCE ACV - DME - MeCN - Bu_4NClO_4 - SCE (In 0.1M Et_4NClO_4)	[130]

 **144**	–2/–1 –1/0 0/+1	–1.38 –0.77 +0.75	IR at RT R at RT	 1.52	CV - Pt – MeCN - Bu_4NBF_4 - SCE	[140]
 **145**	0/+1	–1.0			P - DME - MeCN - Et_4NClO_4 - Ag/Ag$^+$	[59]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

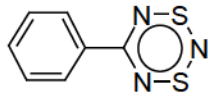
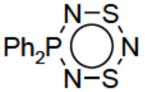
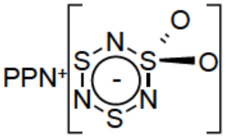
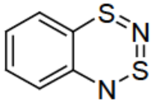
[d] $\bullet E_{cell}\bullet = \bullet E_{ox} - E_{red}\bullet$; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

[f] Internal Fc/Fc$^+$ with pseudo-reference electrode converted to SCE scale using +0.48 as the conversion factor in CH_2Cl_2.

Table 10.

Electrochemical data for Dithiatriazines and Dithiadiazines

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **146**	–1/0	–0.52 p_c	IR at RT		CV - Pt - MeCN - Bu_4NBF_4 - Ag/Ag^{+} [f]	[41]
	0/+1	+1.3				
 **147**	–1/0	–1.10			P - DME - MeCN - Bu_4NClO_4 - SCE	[62] [59]
 **148**	–3/–1	–1.63	R (also studied on RPE and by CV)		P - DME - MeCN - Et_4NClO_4 - Ag/Ag^{+}	[62]
	–1/0	–0.06				
 **149**	–2/–1	–1.55			P - DME - MeCN - Et_4NClO_4 - SCE	[141]
	–1/0	–0.57	R at RT	1.74	P - RPE - MeCN - Et_4NClO_4 - SCE	
	0/+1	+1.17	R at RT			

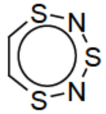
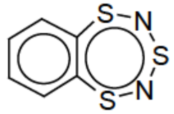
[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.
[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.
[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.
[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

[f] Ag/Ag^+ reference electrode calibrated to the SCE scale.

Table 11.

Electrochemical data for Trithiadiazepines

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **150**	–1/0 0/+1	–1.69 p_c +1.85 p_a	IR at RT IR at RT	3.54	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[89]
 **151**	–1/0 0/+1	–0.83 +1.36	Reduction Oxidation	2.19	P - DME - MeCN - Et_4NClO_4 - SCE P - RPE - MeCN - Et_4NClO_4 - SCE	[141]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

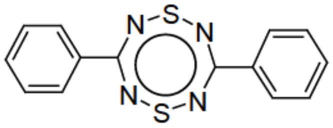
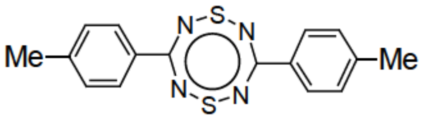
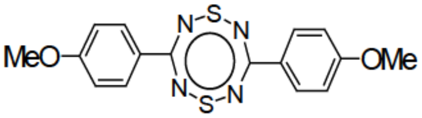
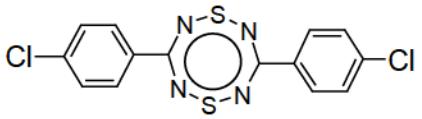
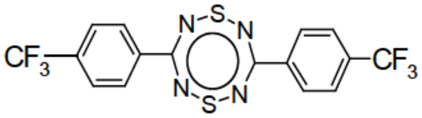
[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

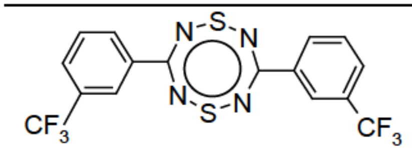
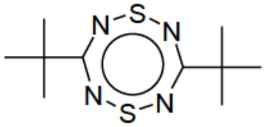
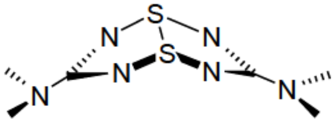
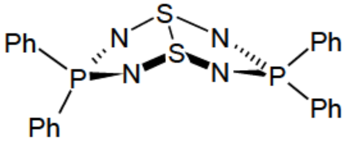
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

[f] Internal Fc/Fc^+ with pseudo-reference electrode converted to SCE scale using +0.48 as the conversion factor in CH_2Cl_2.

Table 12.

Electrochemical data for Dithiatetrazocines

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **152**	–1/0 0/+1	–1.02 +1.86	R at RT QR, $p_a - p_c$ =100mV at • = 200mV s^{-1} and 0°C	2.88	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[31]
 **153**	–1/0 0/+1	–0.90 +1.70	R at RT QR, $p_a - p_c$ = 120mV at • = 500mV s^{-1} and –10°C	2.60	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[31]
 **154**	–1/0 0/+1	–0.95 +1.50	R at RT QR, $p_a - p_c$ = 80mV at • = 200mV s^{-1} and –20°C	2.45	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[31]
 **155**	–1/0 0/+1	–0.98 +1.69	R at RT p_a, IR at RT	2.62	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[31]
 **156**	–1/0 0/+1	–0.91 +2.05	R at RT p_a, IR at RT	2.91	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f]	[31]

 **157**	–1/0	–0.91	R at RT	2.89	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE	[31]
	0/+1	+1.93	QR, $p_a – p_c$ = 100mV at • = 200mV s^{-1} and –10°C		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	
 **158**	–1/0	–1.14	R at RT	2.83	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE	[31]
	0/+1	+1.74	p_a, IR at RT		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	
 **159**	–1/0	–1.36	R at RT	2.59	ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE	[31]
	0/+1	+1.28 p_a	IR at RT		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE^f	
 **160**	–1/0	–1.37	R, radical decays 2-3 s		CV - Pt - MeCN - Et_4NClO_4 - SCE	[110]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

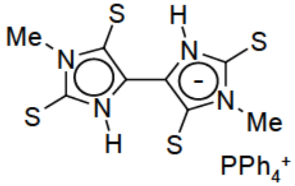
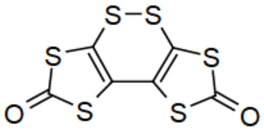
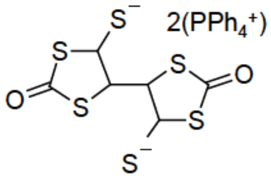
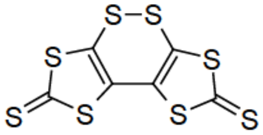
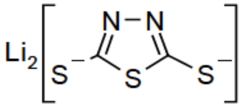
[d] • E_{cell}• = • $E_{ox} – E_{red}$• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

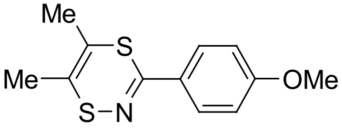
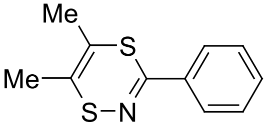
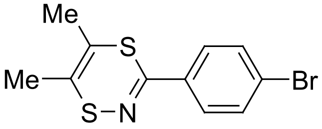
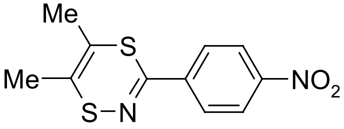
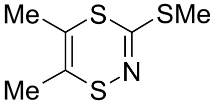
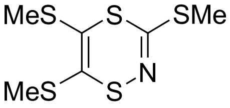
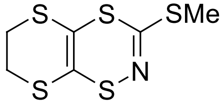
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

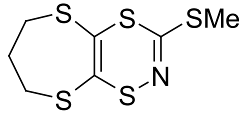
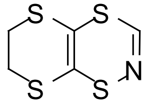
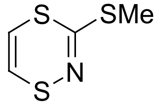
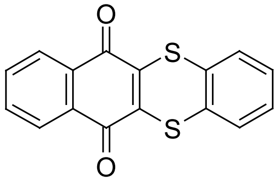
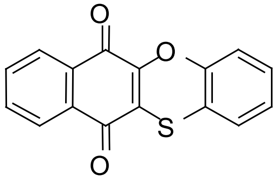
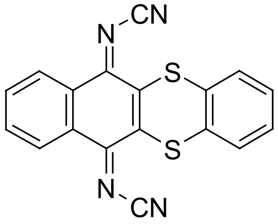
[f] Internal Fc/Fc^+ with pseudo-reference electrode converted to SCE scale using +0.48 as the conversion factor in CH_2Cl_2.

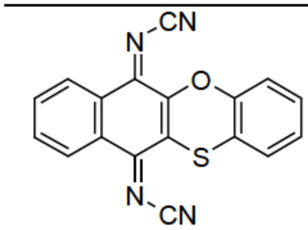
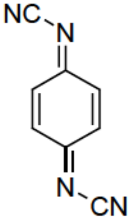
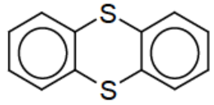
Table 13.

Electrochemical data for Miscellaneous Rings

Compound	Process [a]	Potentials (V) [b]	Comments [c]	• E_{cell}• (V) [d]	Experimental details [e]	Ref.
 **161**	–2/–1 –1/0	–0.482 0.00	R at RT, • = 200 mV/s R at RT, • = 200 mV/s	0.48	CV - Pt - MeCN - Et_4NBF_4 - Ag/AgCl (Internal Fc/Fc$^+$ standard at +0.55 V)	[112]
 **162**	–2/–1 –1/0	–0.21 –0.07	R at RT, • = 100 mV/s R at RT, • = 100 mV/s	0.14	CV - GC - DMF - Bu_4NPF_6 - SSCE [f] DPV - GC - DMF - Bu_4NPF_6 - SSCE (both techniques used for both processes)	[113]
	–2/–1 –1/0	–0.21 –0.07	R at RT, • = 100 mV/s R at RT, • = 100 mV/s	0.14	CV - GC - DMF - Bu_4NPF_6 - SSCE DPV - GC - DMF - Bu_4NPF_6 - SSCE (both techniques used for both processes)	[113]
 **163**	–2/–1 –1/0	–0.06 +0.09	R at RT, • = 100 mV/s R at RT, • = 100 mV/s	0.15	CV - GC - DMF - Bu_4NPF_6 - SSCE DPV - GC - DMF - Bu_4NPF_6 - SSCE (both techniques used for both processes)	[113]
 **164**	–2/–1	–0.3 p_c	Forms S–S bonded dimer; re-reduced at –1.1V		CV - Pt - MeCN - $LiCF_3SO_3$ - Ag/Ag$^+$	[114]

 **165**	0/+1 +1/+2	+1.05 +1.70 p_a	R at RT IR, comproportionation	0.66	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **166**	0/+1 +1/+2	+1.14 +1.72 p_a	R at RT IR, comproportionation	0.58	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **167**	0/+1 +1/+2	+1.15 +1.72 p_a	R at RT IR, comproportionation	0.57	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **168**	0/+1	+1.20	R at RT		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **169**	0/+1	+1.03 p_a	IR		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **170**	0/+1 +1/+2	+1.12 +1.43 p_a	R at RT IR, comproportionation	0.31	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **171**	0/+1 +1/+2	+1.17 +1.58 p_a	R at RT IR, comproportionation	0.41	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]

 **172**	0/+1 +1/+2	+1.22 +1.57 p_a	R at RT IR, comproportionation	0.35	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **173**	0/+1 +1/+2	+1.20 +1.52 p_a	R at RT IR, comproportionation	0.32	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **174**	 0/+1	+1.39 p_a +0.83 p_c	IR but chemically rev		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - Ag/AgCl	[115]
 **175**	–2/–1 –1/0 0/+1	–1.09 –0.53 +1.41 p_a	R at RT R at RT IR	0.56	CV - [g] - CH_2Cl_2 - Bu_4NClO_4 - SCE	[116]
 **176**	–2/–1 –1/0 0/+1	–1.09 –0.59 +1.52 p_a	R at RT R at RT IR	0.50	CV - [g] - CH_2Cl_2 - Bu_4NClO_4 - SCE	[116]
 **177**	–2/–1 –1/0 0/+1	–0.36 0.05 1.51 p_a	R at RT R at RT IR	0.41	CV - [g] - CH_2Cl_2 - Bu_4NClO_4 - SCE	[116]

 **178**	–2/–1 –1/0 0/+1	–0.42 +0.03 1.64 p_a	R at RT R at RT IR	0.45	CV - [g] - CH_2Cl_2 - Bu_4NClO_4 - SCE	[116]
 **179**	–2/–1 –1/0	–0.41 +0.21	R at RT R at RT	0.62	CV - [g] - CH_2Cl_2 - Bu_4NClO_4 - SCE	[116]
 **180**	0/+1 +1/+2 +2/+3	+1.30 +1.65 p_a +1.78 p_a	R at RT IR at RT IR at RT	0.35	CV - GC - MeCN - Bu_4NClO_4 - SCE	[117]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

[d] • E_{cell}• = • E_{ox} – E_{red}• ; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

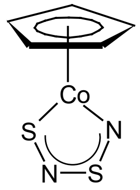
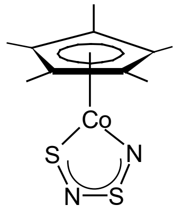
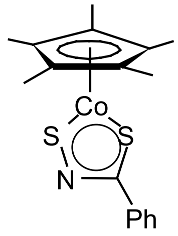
[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

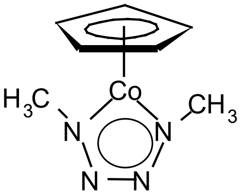
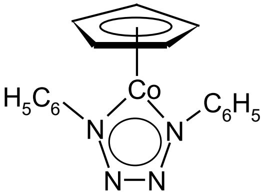
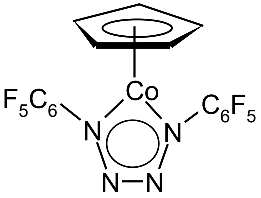
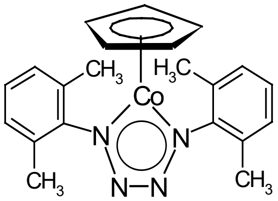
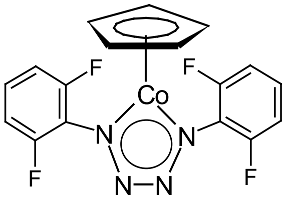
[f] SSCE is the saturated sodium calomel electrode.

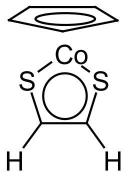
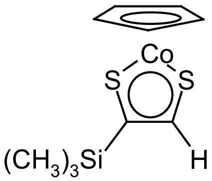
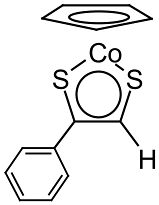
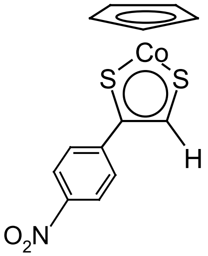
[g] Electrode not specified

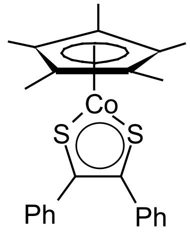
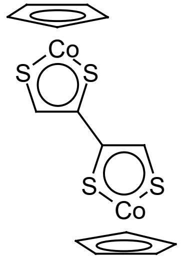
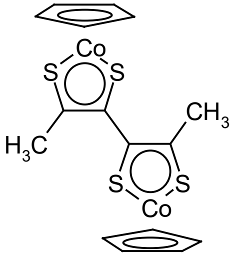
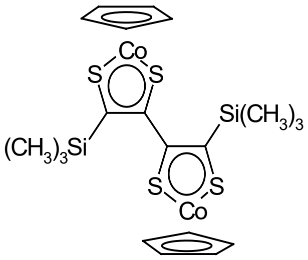
Table 14.

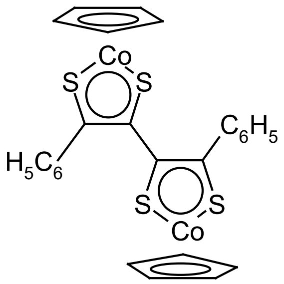
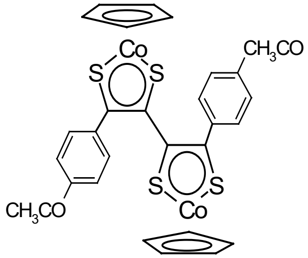
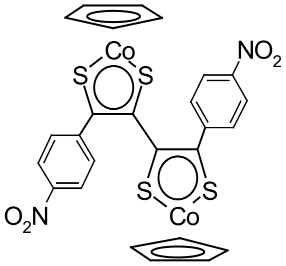
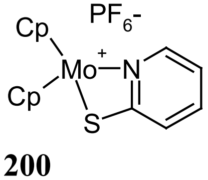
Electrochemical data for Metallacycles

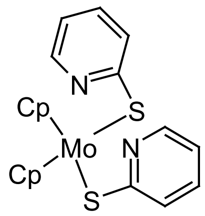
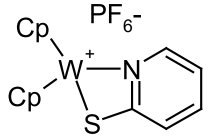
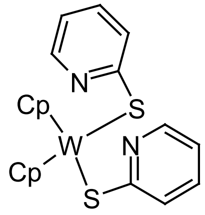
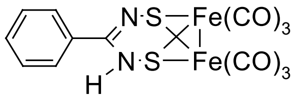
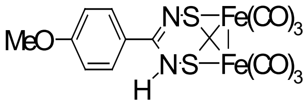
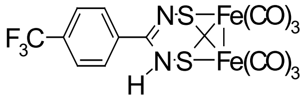
Compound	Process [a]	Potentials (V) [b]	Comments [c]	E_{cell} (V) [d]	Experimental details [e]	Ref.
 **181**	–1/0	–0.65	R by CV (–0.66, R by ACV)		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f] ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE [f]	[32]
 **182**	–1/0	–0.99	QR by CV (–1.02, QR by ACV)		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE [f] ACV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE [f]	[32]
 **183**	–1/0 0/+1	–1.34 +0.4 p_a	R at RT IR at RT		CV - Pt - MeCN - Bu_4NClO_4 - $Ag/AgClO_4$	[142]

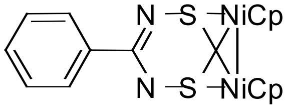
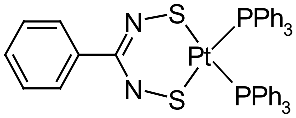
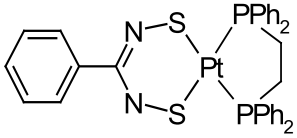
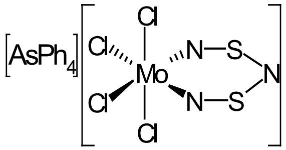
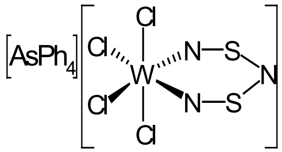
 **184**	–1/0 0/+1 +1/+2	–1.53 +0.89 p_a +1.59 p_a	QR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1}	2.42	CV - Pt - MeCN - Bu$_4$NBF$_4$ - NHE	[143]
 **185**	–1/0 0/+1 +1/+2	–1.01 +0.79 p_a +0.92 p_a	QR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1}	1.80	CV - Pt - MeCN - Bu$_4$NBF$_4$ - NHE	[143]
 **186**	–1/0	–0.70	QR at RT, 200 mV s^{-1}		CV - Pt - MeCN - Bu$_4$NBF$_4$ - NHE	[143]
 **187**	–1/0 0/+1	–1.31 +1.36 p_a	QR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1}	2.67	CV - Pt - MeCN - Bu$_4$NBF$_4$ - NHE	[143]
	–1/0 0/+1	–0.97 +1.24 p_a	QR at RT, 200 mV s^{-1} IR at RT, 200 mV s^{-1}	2.21	CV - Pt - MeCN - Bu$_4$NBF$_4$ - NHE	[143]

188					
 **189**	–1/0	–0.790	R at RT	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - Ag/$AgClO_4$	[118]
 **190**	–1/0	–0.810	R at RT	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - Ag/$AgClO_4$	[118]
 **191**	–1/0	–0.760	R at RT	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - Ag/$AgClO_4$	[118]
 **192**	–1/0	–0.630	R at RT	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - Ag/$AgClO_4$	[118]

 **193**	–1/0	–1.55	R at RT		CV - Pt - MeCN - Bu_4NClO_4 - $Ag/AgClO_4$	[142]
 **194**	–2/–1 –1/0	–0.950 –0.665	R at RT R at RT Irreversibly oxidized at +0.8–1.2 V	0.285	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]
 **195**	–2/–1 –1/0	–1.040 –0.818	R at RT R at RT	0.222	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]
 **196**	–2/–1 –1/0	–1.090 –0.828	R at RT R at RT	0.262	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]

 **197**	–2/–1 –1/0	–0.880 –0.720	R at RT R at RT	0.16	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]
 **198**	–2/–1 –1/0	–0.876 –0.682	R at RT R at RT	0.194	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]
 **199**	–2/–1 –1/0	–0.810 –0.610	R at RT R at RT	0.200	CV - Pt - CH_2Cl_2 - Bu_4NClO_4 - $Ag/AgClO_4$	[118]
 **200**	0/+1	+1.24	Quasi-reversible, dependent on switching potential		CV - Pt - MeCN - Bu_4NPF_6 - SCE	[119]

 **201**	0/+1	+0.38	Quasi-reversible, dependent on switching potential	CV - Pt - MeCN - Bu_4NPF_6 - SCE	[119]
 **202**	0/+1	+1.23	Quasi-reversible, dependent on switching potential	CV - Pt - MeCN - Bu_4NPF_6 - SCE	[119]
 **203**	0/+1	+0.33	Quasi-reversible, dependent on switching potential	CV - Pt - MeCN - Bu_4NPF_6 - SCE	[119]
 **204**	–1/0 0/+1	–1.70 +1.2 p_a	R at 25^{o}C IR at T up to $–50^{o}$C and 10 V s^{-1}	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{f}	[33,144]
 **205**	–1/0 0/+1	–1.69 +1.0 p_a	R at 200 mV s^{-1}, $–20^{o}$C IR at v = 50-1000 mV s^{-1}, 25^{o}C	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{f}	[33,144]
 **206**	–1/0 0/+1	–1.57 +1.3 p_a	R at 200 mV s^{-1}, $–20^{o}$C IR at v = 50-1000 mV s^{-1}, 25^{o}C	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE ^{f}	[33,144]

 **207**	–1/0 0/+1 +1/+2	–0.79 +0.45 +1.9 p_a	R at RT R at RT IR at v = 50-1000 mV s^{-1}, 25°C	1.24	CV - Pt - CH_2Cl_2 - Bu_4NPF_6 - SCE[f]	[33,144]
 **208**	–1/0 0/+1	–1.04 +0.01	R at RT R at RT	1.05	CV - Pt - MeCN - Bu_4NBF_4 – SCE[g]	[121]
 **209**	–1/0 0/+1	–1.66 p_c +0.10	IR at RT R at RT	1.76	CV - Pt - MeCN - Bu_4NBF_4 – SCE[g]	[121]
 **210**	–3/–2 –2/–1	–0.68 +0.62	IR in CV (p_a = –0.8, –0.68 by ACV) R at RT (R by ACV)		CV - Pt - CH_2Cl_2 - Bu_4NPF_6 – SCE[f]	[34]
 **211**	–3/–2 –2/–1	–1.19 +0.09	IR in CV (p_a = –1.19, –0.68 by ACV) R at RT (R by ACV)		CV – Pt – CH_2Cl_2 – Bu_4NPF_6 – SCE[f]	[34]

[a] Expressed in terms of the (reversible) redox couples, starting with the most negative potential in accordance with current IUPAC recommendations.

[b] Expressed as the half-wave potential from polarography, or the difference between p_c and p_a from cyclic voltammetry, for reversible systems, unless otherwise noted.

[c] R = reversible; IR = irreversible; QR = quasi-reversible; other comments as required.

[d] $\bullet E_{cell}\bullet = \bullet E_{ox} - E_{red}\bullet$; corresponds to a disproportionation energy when the conditions of Equation 1 are satisfied.

[e] Technique (P = polarography, CV = cyclic voltammetry, DPV = differential pulse voltammetry, ACV = a.c. voltammetry EL = electrolysis) – Electrode type (DME = dropping mercury electrode, RPE = rotating platinum electrode, Pt = platinum, GC = glassy carbon) – solvent (MeCN = acetonitrile, CH_2Cl_2 = dichloromethane, DMF = dimethylformamide, SO_2 = sulfur dioxide) – Electrolyte - Reference electrode system for data (if the actual reference electrode used is different from the quoted system, a note is given in the footnotes.)

[f] Internal Fc/Fc^+ with pseudo-reference electrode converted to SCE scale using +0.48 as the conversion factor in CH_2Cl_2.
system

[g] Ag/Ag^+ reference electrode calibrated to the SCE scale.