Solution Disproportionation Energies of 1,2,3,5-Dithia- and Diselenadiazoles. Direct Comparison of Solution Oxidation Potentials with Ionization Energies in the Gas Phase[1]

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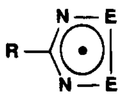
Abstract: Cyclic and ac voltammetry were carried out on 17 different 1,2,3,5-dithia- or diselenadiazole radicals under vacuum in CH_2Cl_2 and CH_3CN solutions containing NBu_4PF_6 electrolyte. The redox potentials for the oxidation and reduction processes are reported, referenced to SCE using ferrocene as a secondary standard. The oxidation process for five of the dithiadiazole radicals correlates linearly with the gas-phase ionization energies previously obtained from UV-PES, and the damping influence of the solvent medium is evident. Disproportionation energies defined as $\mathcal{E}_{\rm cell} = -\{\mathcal{E}^{\rm oxid} - \mathcal{E}^{\rm reduc}\}$ were calculated: (E = S, -1.43 ± 0.06 V in CH_3CN and -1.61 ± 0.06 V in CH_2Cl_2 (average of 11 compounds); E = Se, -1.25 ± 0.03 in CH_3CN and -1.39 ± 0.05 V in CH_2Cl_2 (average of six compounds)) and compared to the enthalpies of the same process in the gas phase obtained from MNDO calculations ($\mathcal{E}_{\rm cell}(\rm gas) = -6.5$ V). Both calculation and experiment show that the title compounds, by comparison with TTF^+, $TCNQ^-$, and other related compounds, have higher than desirable disproportionation energies which is a disadvantage for their use in constructing molecular metals. The electrochemistry of 1,4-bis(dithia- and diselenadiazolyl)benzene has also been investigated by voltammetry and coulometry. These bifunctional diradicals undergo independent redox chemistry in each CN_2E_2 ring, and the "oxidation" process involves a two-electron transfer confirmed by coulometry. The disproportionation energies of these compounds are shown to be similar to those of the monofunctional radicals; by implication the same limitations apply to their solid-state properties.

Introduction

1,2,3,5-Dithia- and diselenadiazoles, **1**, have come closer to the realization of intrinsic molecular conductors built from stable neutral π-radicals than any system of this type.[2,3] The hypothesis that superior molecular conductors could be built from such systems, which can exist in a triad of oxidation states, was first advanced by Haddon.[4] Initially odd-alternant hydrocarbons such as the phenalenyl radical, **2**,[5] were considered for this application.



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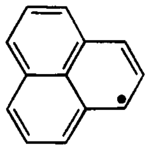

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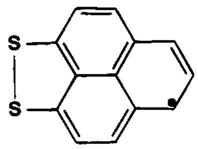

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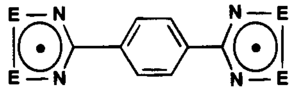
Later a variety of heteroatom substituted derivatives were also investigated by Haddon and others,[6] for example, the dithiaderivative **3**.[6d] One of the chief design factors sought in such materials is weak electron-electron (coulombic) repulsion, since this can be correlated with minimization of 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

$$2\ \text{radical} \rightleftharpoons \text{cation}^+ + \text{anion}^- \qquad (1)$$

the free energy should be as small as possible. This criterion was originally assessed using estimates of the enthalpies of the gas-phase reaction obtained from MINDO/3 calculations.[4] On this basis **2** was found to have comparable disproportionation energy to the well-known charge-transfer salt components TTF^+ and $TCNQ^-$. **2** and **3** were found to be limited for building conductors by a strong tendency to dimerize through C–C bond formation, even in solution.[6d,7] Radicals of type **1**, where the spin density is distributed over two chalcogen and two nitrogen atoms, form weak dimers through the chalcogen atoms in the solid state. The dimers do not persist in solution. Specific derivatives of **1** with suitable intra- and interstack interactions, intended to minimize Peierls distortions in the solid state,[3] have been found to be intrinsic semiconductors. For example **1, E = Se, R = H** has a RT conductivity $\sigma = 7 \times 10^{-6}$ S cm^{-1};[2g] **4, E = Se,** $\sigma = 1 \times 10^{-2}$ S cm^{-1} (the corresponding sulfur compound is an insulator);[2m] **5, E = Se,** α-phase $\sigma = 2 \times 10^{-4}$ S cm^{-1};[2l] β-phase $\sigma = 1 \times 10^{-4}$ S cm^{-1} (again with E = S an insulator),[2h] while the sulfur compound 1,3,5-$\{S_2N_2C\}_3C_6H_3$, for which the Se analog could not be prepared, has $\sigma = 1 \times 10^{-7}$ S cm^{-1}.[2j]



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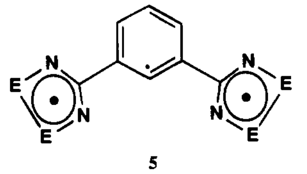

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Solution electrochemistry is an obvious source of experimental disproportionation energies.[8] This work is concerned

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[1] Part of this work was presented at the 7th International Symposium on Ring Systems (IRIS), Banff, Canada, August, 1994.

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with the measurement of the solution-phase free energies of disproportionation of **1** as a function of substituent and solvent using cyclic voltammetry. We compare these condensed-phase results with gas-phase energies calculated by Haddon's method. As expected there are large differences between gas-phase estimates and experimental data in solution. As one check on this difference we were able to compare directly the gas-phase ionization of numerous dithiadiazoles **1, E = S**, previously obtained by UV-PES,[9] with the solution-phase oxidation process. (Lack of experimental electron affinities makes it impossible to obtain such a comparison for the reductions.) The correlation between the two sets of data is found to be linear, and the profound damping effect of the solvent medium is clearly demonstrated.

True metallic behavior has not been found for any derivatives of **1** because of their instability to a Peierls distortion.[3] Such instability is maximized for the half-filled band implicit in using neutral radicals to build a molecular metal. Very recently derivatives of **1** as well as the bifunctional analogs **4** and **5** have been rendered metallic by partial oxidation using molecular iodine.[10] Electrochemical data is therefore also of practical value for selecting specific oxidizing agents which are suitable for the doping reactions. We have also studied the electrochemistryd of **4** and demonstrate independent redox processes at the two CN_2E_2 rings.

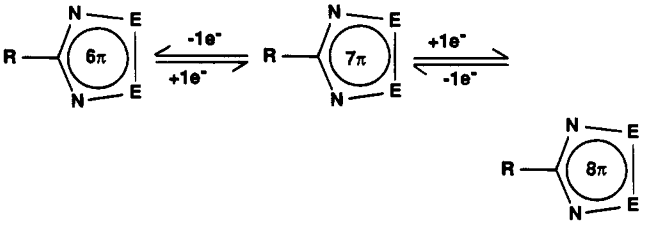
Results and Discussion

Voltammetric Methodology and Results. We have employed solution electrochemistry by cyclic voltammetry (cv) and phase-sensitive alternating current (ac) voltammetry. As we recently reported for a series of substituted aryl derivatives of **1**, it is preferable for this class of compound to start out with the neutral radicals as the bulk form in solution.[11] An irreversible second reduction is observed in most cases when the starting material is a salt of the cation; i.e.; $1^+MF_6^-$ (M = P, As, Sb). It has been proposed that this is due to a rapid conproportionation reaction[12]

$$1^- + 1^+ \rightarrow 2\,1\cdot \qquad (2)$$

In our experience use of solutions made up from vacuum-sublimed dimer of the free-radicals overcomes this problem. We have found absolutely no evidence that any derivatives of type **1** retain their dimeric structure in solution, and all the electrochemical processes can safely be attributed to the monomeric species.[13] The non-aryl substituted rings reported in this work are even more sensitive than the aryl compounds toward reaction with oxygen as well as being moisture sensitive and in some cases (R = CF_3, E = Se) also photosensitive; consequently the electrochemical experiments were conducted in an all-glass electrochemical cell under vacuum using break-seal techniques for loading the reagents and vacuum transfer of the solvents.[14]

The results of the electrochemical investigations are compiled in Tables 1−3. In most cases we found both reversible oxidation and reversible reduction, so that the redox process can be summarized.



Exceptions were found in the case R = $CF_3C_6H_4$, E = S and R = CF_3, E = S, which undergo irreversible reduction, but the processes for their selenium analogs are reversible. For R = Cl, E = S the anion underwent rapid chemical decomposition and waves resulting from the decomposition products were observable. Prolonged reduction resulted in production of a brown precipitate of undetermined composition. When both the reduction and oxidation potentials can be measured reversibly, the disproportionation energy, defined as $\mathcal{E}_{\text{cell}}$ for reaction 1, can be calculated with confidence.[15] Values obtained from quasi-reversible or irreversible reductions are marked with

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Table 1. Voltammetric Data for 1,2,3,4-Dithia- and Diselenadiazoles

R =	ref[a]	oxidation $\mathcal{E}_{1/2}$,[b] (V)	reduction $\mathcal{E}_{1/2}$,[b] (V)	$\mathcal{E}_{cell}$,[c] (V)	IE[d] (eV)
E = S, CH_3CN Solution[e]					
Me_2N	25	+0.35	−0.96	−1.31	7.10[f]
CH_3	26	+0.59	−0.94	−1.53	
Ph[g]	27	+0.60	−0.83	−1.43	7.40[h]
2-furyl	28	+0.63	−0.79	−1.42	
H	2b	+0.65	−0.83	−1.48	7.87[i]
Cl	28, 29	+0.83	−0.63[j]	−1.46*	8.00[h]
CF_3	30	+0.91	−0.42[k]	1.33*	8.25[h]
E = Se, CH_3CN Solution[e]					
Ph[g]	2n	+0.63	−0.61	−1.24	
CF_3	31	+0.89	−0.41	−1.30	
E = S, CH_2Cl_2 Solution[l]					
Me_2N	25	+0.50	−0.95[m]	−1.45*	7.10[f]
CH_3	25	+0.78	−0.88	−1.66	
Ph[g]	27	+0.78	−0.82	−1.60	7.40[h]
2-furyl	28	+0.84	−0.81[n]	−1.65*	
H	2b	+0.86	−0.81[m]	−1.67*	7.87[i]
Cl	28,29	+1.04	−0.64[o]	−1.68*	8.00[h]
CF_3	30	+1.11	−0.48[p]	−1.59*	8.25[h]
E = Se, CH_2Cl_2 Solution[l]					
Ph[g]	2n	+0.79	−0.59	−1.38	
CF_3	31	+1.11	−0.39	−1.49	

[a] Synthesis and structure of the neutral dimer, from which the radical is obtained in solution. [b] Reversible conditions at a scan rate $\nu = 100$ mV s^{-1} at 25 °C, unless otherwise noted. [c] Disproportionation potential defined as $-\{\mathcal{E}^{oxid} - \mathcal{E}^{reduc}\}$. $\mathcal{E}_{cell}$ not obtained from fully reversible oxidation and reduction processes are marked with an asterisk (*). [d] Vertical ionization potentials from UV-PES measurements. [e] At a Pt-electrode in CH_3CN containing 0.1 M NBu_4PF_6 electrolyte, referenced to SCE such that $\mathcal{E}_{1/2} = +0.38$ V for $[Cp_2Fe]^{+/0}$. [f] From ref 25. [g] From ref 11. [h] From ref 9. [i] From ref 2b. [j] Irreversible behavior ($\mathcal{E}_c$, with $\nu = 10$ Vs^{-1}), new feature appears at $\mathcal{E}_{1/2} = +0.59$ V. [k] Irreversible behavior ($\mathcal{E}_c$, with $\nu = 200$ mVs^{-1} at −20 °C). [l] At a Pt-electrode in CH_2Cl_2 containing 0.5 M NBu_4PF_6 electrolyte, referenced to SCE such that $\mathcal{E}_{1/2} = +0.48$ V for $[Cp_2Fe]^{+/0}$. [m] Quasi reversible behavior, $\mathcal{E}_a - \mathcal{E}_c = 250$ mV at $\nu = 200$ mV s^{-1} and +25 °C. [n] Quasi reversible behavior, $\mathcal{E}_a - \mathcal{E}_c = 150$ mV at $\nu = 200$ mV s^{-1} and +25 °C. [o] Irreversible behavior, $\mathcal{E}_c$, new feature appears at $\mathcal{E}_{1/2} = +0.6$ V. [p] Reversible conditions at $\nu = 500$ mV s^{-1} and +25 °C.

Table 2. Redox Potentials of Aryl Dithia- and Diselenadiazoles[a]

R =	oxidation $\mathcal{E}_{1/2}$ (V)	reduction $\mathcal{E}_{1/2}$, (V)	$\mathcal{E}_{cell}$,[b] (V)
E = S, CH_3CN Solution			
$4\text{-}CH_3OC_6H_4$	+0.57	−0.87	−1.44
$4\text{-}CH_3C_6H_4$	+0.59	−0.89	−1.48
C_6H_5	+0.60	−0.83	−1.43
$4\text{-}ClC_6H_4$	+0.62	−0.81	−1.43
$4\text{-}CF_3C_6H_4$	+0.66	−0.80[c]	−1.46*
E = Se, CH_3CN Solution			
$4\text{-}CH_3OC_6H_4$	+0.57	−0.68[d]	−1.25*
$4\text{-}CH_3C_6H_4$	+0.62	−0.61[d]	−1.23*
C_6H_5	+0.63	−0.61[d]	−1.24*
$4\text{-}ClC_6H_4$	+0.64	−0.59[d]	−1.23*
$4\text{-}CF_3C_6H_4$	+0.67	−0.57[c]	−1.24*
E = S, CH_2Cl_2 Solution			
$4\text{-}CH_3OC_6H_4$	+0.73	−0.85	−1.58
$4\text{-}CH_3C_6H_4$	+0.77	−0.83	−1.60
C_6H_5	+0.78	−0.82	−1.60
$4\text{-}ClC_6H_4$	+0.82	−0.78	−1.60
$4\text{-}CF_3C_6H_4$	+0.86	−0.73[c]	−1.59*
E = Se, CH_2Cl_2 Solution			
$4\text{-}CH_3OC_6H_4$	+0.74	−0.61	−1.35
$4\text{-}CH_3C_6H_4$	+0.77	−0.57	−1.34
C_6H_5	+0.79	−0.59	−1.38
$4\text{-}ClC_6H_4$	+0.82	−0.55	−1.37
$4\text{-}CF_3C_6H_4$	+0.86	−0.53	−1.39

[a] Full details of the synthesis, structures, and electrochemical measurements for these compounds have been previously reported (ref 11), and only the potential data are presented here. $\mathcal{E}_{cell}$ not obtained from fully reversible oxidation and reduction processes are marked with an asterisk (*). [b] Disproportionation potential defined as $-\{\mathcal{E}^{oxid} - \mathcal{E}^{reduc}\}$. [c] Irreversible behavior. [d] Quasireversible behavior.

Table 3. Voltammetric Data for Bifunctional Compounds[a]

		oxidation		reduction		
compd		$\mathcal{E}_{1/2}$ (V)	sep'n[b] (mV)	$\mathcal{E}_{1/2}$ (V)	sep'n[b] (mV)	$\mathcal{E}_{cell}$[c] (V)
CH_3CN Solution[d]						
4a[e]	E = S	+0.61	33	−0.80	80	−1.41
4b[f]	E = Se	+0.75	45	−0.63	83	−1.38
CH_2Cl_2 solution[g]						
4a[h]	E = S[i]	+0.78	30	−0.72	85	−1.50

[a] Reversible conditions at a scan rate $\nu = 100$ mV s^{-1} at 25 °C, unless otherwise noted. [b] Separation between anodic ($\mathcal{E}_a$) and cathodic ($\mathcal{E}_c$) peak. [c] Disproportionation energy defined as $-\{\mathcal{E}^{oxid} - \mathcal{E}^{reduc}\}$. [d] At a Pt-electrode in CH_3CN containing 0.1 M NBu_4PF_6 electrolyte, referenced to SCE such that $\mathcal{E}_{1/2} = +0.38$ V for $[Cp_2Fe]^{+/0}$. [e] Measured from the salt $[1,4\text{-}(S_2N_2C)_2C_6H_4][SbF_6]_2\cdot[PhCN]_2$; synthesis ref 2m; structure ref 32. [f] Measured from the salt $[1,4\text{-}(Se_2N_2C)_2\text{-}C_6H_4][SbF_6]_2\cdot[PhCN]_3$; synthesis ref 2m; structure ref 33. [g] At a Pt-electrode in CH_2Cl_2 containing 0.5 M NBu_4PF_6 electrolyte, referenced to SCE such that $\mathcal{E}_{1/2} = +0.48$ V for $[Cp_2Fe]^{+/0}$. [h] Measured from the dimer of the neutral radical; synthesis and structure ref 2m. [i] E = Se was insufficiently soluble in this solvent to measure.

asterisks in the data tables. It becomes apparent from this extensive series of compounds that very little error is introduced by these, especially the quasi-reversible cases for which a return wave could be observed in the electrochemical experiment by cooling and/or fast-scanning. However we could not have been confident of this if we had not measured such a series.

Summary of Potential Data for Monofunctional Radicals. The substituent influence is small. It ranges over less than 0.1 V for a variety of 4-aryl-substituted derivatives (Table 2) for measurements in CH_3CN and about 0.5 V for substituents directly attached to the dichalcogenadiazole ring, from the strongly electron-donating dimethylamino group to the extremely strong electron withdrawing CF_3 (Table 1). The range is slightly higher for both groups of compounds in CH_2Cl_2 (0.13 and 0.61 V, respectively).

$\mathcal{E}_{cell}$ is extremely similar for all substituents (Tables 1−3). That is to say that on the whole the substituent affects both the oxidation and the reduction potentials to the same extent. The measured cell potentials can be averaged as follows: **1, E = S,** −1.43 ± 0.06 V in CH_3CN and −1.61 ± 0.06 V in CH_2Cl_2 (average of 11 compounds); **1, E = Se,** −1.25 ± 0.03 V in CH_3CN and −1.39 ± 0.05 V in CH_2Cl_2 (average of six compounds). The only striking deviation is for R = NMe_2, which has a significantly smaller value in both solvents (−1.45 V in methylene chloride and −1.31 V in acetonitrile). There are several other cases where the strong donor influence of the dimethylamino substituent on C, N, S heterocycles has been observed.[16] This deviation is ascribable to a facile oxidation of the dimethylamino derivative,[17] whereas the reduction potential is shifted less from values observed for other dithiadiazoles. When S is replaced by Se, $\mathcal{E}_{cell}$ fall by *ca.* 0.2 V in both solvents.

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(13) In contrast to 1, high dimer concentrations exist in solution for 1,2,4,6-thiatriazines (by ESR: Bestari, K.; Cordes, A. W.; Oakley, R. T.; Young, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2249) and for 1,3,2,4,6-dithiatriazines (by NMR: Boeré, R. T.; Fait, J.; Larsen, K; Yip, J. *Inorg. Chem.* **1992**, *31*, 1417).

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(15) Brownstein, S.; Heath, G. A.; Sengupta, A.; Sharp, D. W. A. *J. Chem. Soc., Chem. Commun.* **1983**, 669.

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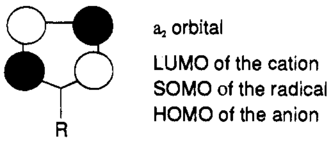
The small variation in substituent effect is nonetheless very well defined. Thus for 4-aryl substituents the oxidation potentials correlate well with Hammet σ parameters[12] as well as with calculated energies of the SOMO by semiempirical methods.[11] Bond has suggested for compounds of similar structure and in the absence of rearrangements triggered by the electrochemical changes, that the redox potentials reflect the energies of the redox orbitals.[18] This is the situation for **1**: all of the above observations are consistent with redox processes involving only a localized SOMO with a node at the carbon atom, the well-known a_2 orbital.



In all cases where identical substituents are involved the replacement of S by Se does not affect the potential of the oxidation process. Thus the lower value for the disproportionation energy in the diselenadiazoles is due to a lower reduction potential in all cases.

The influence of the solvent is larger than the small substituent effect. Thus the magnitude of $\mathcal{E}_{\text{cell}}$ is 0.2 V larger in the less polar solvent CH_2Cl_2 than in CH_3CN. That is to say that the stronger the solvation the smaller the disproportionation energy becomes. Methylene chloride solutions are thus better approximations to the gas-phase behavior, and acetonitrile mimics the solid state better. Of course, these differences are small compared to the drastic effect of moving from the gas to a condensed phase. Nonetheless the necessity of strong interstack interactions has been recognized previously in order to combat a Peierls instability.[2,3] Such interactions may also be important as a solid state analogy to solvation by lowering ionic fluctuations during conduction.

Correlation of Gas-Phase and Solution Ionization Data. In the case of several of the dithiadiazoles reported here it is possible to directly compare the solution oxidation process with the gas-phase ionization energies of the radicals as determined by UV-PES (data in Table 1), to our knowledge the first such correlation for neutral radicals. Figure 1 demonstrates linear correlation between redox potentials measured in CH_2Cl_2 solution and the vertical first ionization energies in the gas phase for five compounds with widely differing substituents. This line can be expressed as $\mathcal{E}_{1/2} = 0.50 \times \text{IE} - 2.98$ V ($r = 0.91$). A very similar plot is obtained using the CH_3CN data: $\mathcal{E}_{1/2} = 0.45 \times \text{IE} - 2.80$ V ($r = 0.89$).

There have been many attempts to devise satisfactory linear correlations between gas-phase and solution ionization energies for organic compounds, using $\mathcal{E}_{1/2}$ measured in CH_3CN.[19] Miller demonstrated a linear correlation fitting the equation $\mathcal{E}_{1/2} = 0.92 \times \text{IE} - 6.20$ V (r = 0.92),[19a] and Parker found even alternant aromatic hydrocarbons to fit $\mathcal{E}_{1/2} = 1.00 \times \text{IE} - 6.36$ V.[19b,c] Sandman reported that a large variety of compounds correlate to the function $\mathcal{E}_{1/2} = 1.00 \times \text{IE} - 6.44$ V ($r = 0.89$),[19d] but this correlation contains considerable scatter. Thus if from Sandman's data only derivatives of TTF (saturated and unsaturated, with substituents ranging from CH_3 to CN, and covering a range of more than 1 eV in ionization energy) are plotted separately, these fit the relationship $\mathcal{E}_{1/2} = 0.51 \times \text{IE} - 3.02$ V ($r = 0.87$). This latter is amazingly close to our results for **1**. A slope of 1.00 in relationships of this type has been postulated as typical for aromatic hydrocarbons and implies that the free energy of solvation of the neutral and cationic forms of such compounds is identical.[19b] Nelsen has noted both large scatter and much smaller slopes than unity for the gas/solution ionization correlation of organic amines;[19e] the deviation is attributed to both reorganizational (i.e., pyramidal to planar nitrogen) and differential solvation effects. Deviations in slope for tetrathiafulvalenes[19d] and related compounds[19f] have been noted. For **1** and tetrathiafulvalenes, reorganization is predicted to be small, implying that the deviations are largely due to differential solvation of the neutral species and the cation; consistently the slopes for these two classes of compounds are $\approxeq 0.5$, while for the amines slopes around 0.2 were found for series of related compounds. Correlations of the type described above have also been attempted between reduction potentials and electron affinities, albeit with calculated values; for aromatic hydrocarbons slopes close to unity are also obtained.[20]

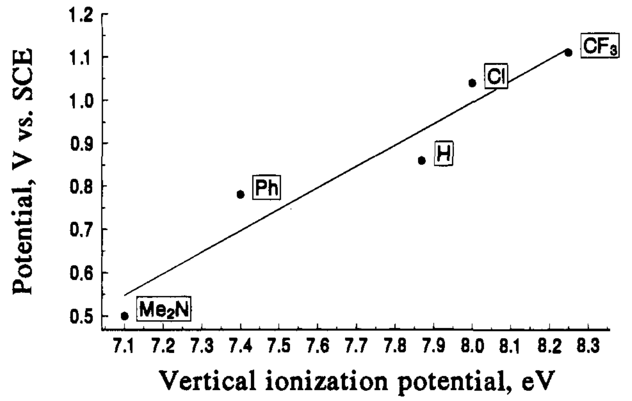


Figure 1. Plot showing the correlation between the ionization energies obtained from UV-PES in the gas phase and the oxidation potential in CH_2Cl_2 solution for five 1,2,3,5-dithiadiazole radicals RCN_2S_2 with the indicated substituents R.

Bifunctional CN_2E_2 Compounds. The bifunctional radicals **4** and **5** are completely insoluble in CH_3CN, but **4**, E = S is sufficiently soluble in CH_2Cl_2 to allow recording of acceptable cyclic voltammograms. In contrast to an earlier report on the first reduction of the dication of **4**, E = S,[2n] we noticed a very small separation between anodic ($\mathcal{E}_a$) and cathodic ($\mathcal{E}_c$) peaks of only 30 mV for this process. We have therefore also measured the dications of **4** starting from their SbF_6^- salts, which crystallize as benzonitrile adducts. These salts have good solubility in CH_3CN but are totally insoluble in CH_2Cl_2. Acceptable cv's were obtained starting from either source after considerable effort, even for the "reduction" process (i.e., the second reduction starting from the dication, leading to the dianion). In particular low solute concentrations in an exceptionally pure solvent/electrolyte mixture are required. This means that we are able to compare potentials for **4** for the two solvents used in our study of the monofunctional heterocycles. The data we have been able to obtain are summarized in Table 3.

The results of the measurements in the two solvents, i.e., of the dications in CH_3CN and the diradicals in CH_2Cl_2, present a

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(17) We note that the oxidation potential of this compound brings it within the range of redox potentials of those cations which form metallic conductors with TCNQ. Oxidation potentials outside of the narrow range of +0.5–0.0 V vs SCE (in CH_3CN) form at best semiconductor charge-transfer salts with TCNQ. See: Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(18) Bond, A. M.; Dawson, P. A.; Peak, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199.

(19) (a) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (b) Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656. (c) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (d) Sandman, D. J.; Ceasar, G. P. *Israel J. Chem.* **1986**, *27*, 293. (e) Nelsen, S. F. *Israel J. Chem.* **1979**, *18*, 45. (f) Sandman, D. J.; Zoski, G. D.; Burke, A. A.; Hamill, G. P.; Ceasar, G. P.; Baker, A. D. *J. C. S., Chem. Commun.* **1981**, 829.

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uniform picture. Regardless of whether the dication or the diradical is used as the source of the compound, the cyclic voltammograms of **4** contain a single wave for the "oxidation" and a single wave for the "reduction" process. The waves are unusually narrow (30−45 mV) compared to those of all the monoradicals reported in this study, indicative of a possible two electron process. The appearance of the cv's are consistent with a two electron step in which $\Delta E = 0$, producing a single peak with a peak current intermediate between those of a single one electron and two electron reaction.[21] Starting from the dications, we have confirmed two electron transfer for the "oxidation" process of **4** by coulometry in CH_3CN. However, owing to the complete insolubility of the diradicals in this solvent, we have not been able to confirm the number of electrons transferred for the "reduction" process (during electrolysis of the dication crystalline **4** was deposited on the working electrode).

The potentials obtained for **4, E = S** strongly resemble those of **1 (E = S, R = Ph)**. The "oxidation" process measured in CH_3CN is in good agreement with the value of +0.65 previously reported for the AsF_6^- salt.[12] Consequently the $\mathscr{E}_{cell}$ values also strongly resemble those of the monofunctional radicals. There is somewhat more deviation for the CH_2Cl_2 data, and for **4 (E = Se)** the oxidation process in CH_3CN deviates 0.1 V from that of **1 (E = Se, R = Ph)**. In view of the extreme solubility limitations and the necessity of using both salts and the radicals to obtain data in both solvents we do not consider these differences to be meaningful. All of these results are consistent with a redox process constrained to the N_2E_2 ring atoms and thus occurring independently within the two units of a bifunctional radical. Further the "substituent effect" of one CN_2E_2 group on another substituted on a benzene ring is extremely small.[12] Any additional subtle effects which might be present cannot be assessed with species of such low solubility.

Disproportionation Energies. In order to assess the utility of our ϵ_{cell} values, we compare them to gas-phase estimates of other potential molecular metal building blocks for which electrochemical data are available in the same solvent (CH_3CN) and employing similar electrolytes. We have calculated the disproportionation energies in the gas phase of **1**, **2**, **3**, **6**,[22] **7**,[8b] and **8**,[8a] using Haddon's method,[4] but employing MNDO rather than MINDO/3. The results of these calculations are presented in Table 4. Compared to **2, 3, 6−8**, which all have MNDO disproportionation energies of around 400−450 kJ mol^{-1}, **1, R = H** has a much higher calculated value of 653 kJ mol^{-1}.


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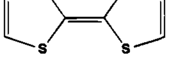
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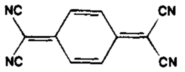
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We have converted gas-phase disproportionation energies to a gas-phase $\mathscr{E}_{cell}$ by equating $\Delta G = \Delta H$ (Table 4).[20] Side-by-side comparison is then possible between the gas-phase estimates and experimental electrochemical measurements, as reported in the literature. The lack of a quantitative correlation between ionization energy and oxidation potentials for compounds of this type noted above argues against attempting any quantitative conversions of $\mathscr{E}_{cell}$. However, the following points are worth considering. The "reduction" process in **6** is electrochemically irreversible, but chemically reversible, and a return oxidation wave was observed in the cyclic voltammogram.[22] If the average of the cathodic and anodic peak potentials for this second reduction of $\mathbf{6}^+$ is used, the apparent cell potential of this compound becomes −0.48 V, in much better agreement with the other data in the table. The second reduction of **2** is also highly irreversible, and very few details of its electrochemistry have been reported.[6d] It is not clear if dimerization of the radical was taken into consideration, or what the chemical fate of the unstable anion is. Thus the equivalent reversible $\mathscr{E}_{cell}$ for **2** could actually be considerably smaller than −1.6 V. We recognize also that **2**, as a symmetric hydrocarbon lacking heteroatoms along its periphery, is structurally the least like the other compounds listed in Table 4. Consequently any differences in $\mathscr{E}_{cell}$ caused by the effects of differential solvation on the redox potentials of the compounds under consideration will be most serious for **2**.

Table 4. Calculated[a] and Measured[b] Disproportionation Energies

compd	rad − *e*, kJ mol^{-1}	radical, kJ mol^{-1}	rad + *e*, kJ mol^{-1}	disp *E*,[c] kJ mol^{-1}	$\mathscr{E}_{cell}$(gas),[d] V	$\mathscr{E}_{cell}$(sol),[e] V
1, R = H	1119	242	18	653	−6.50	−1.48[f]
2	916	270	69	445	−4.61	−1.6[g]
3	946	285	44	421	−4.38	−0.55[h]
6	1032	363	134	440	−4.58	−0.80[i]
$\mathbf{7}^+$	2084	909	171	436	−4.53	−0.37[j]
$\mathbf{8}^-$	782	452	489	368	−3.83	−0.42[k]

[a] Calculational method defined in ref 4; MNDO method used in the program HyperChem (ref 23). [b] From cyclic voltammetry in CH_3CN solutions containing an inert electrolyte. [c] Disp E = {E(rad − *e*) + E(rad + *e*)} − 2 E(radical). [d] $\mathscr{E}_{cell}$(gas) = (Disp E × 1000)/(N_A × *e*), ignoring any contribution from entropy. [e] $\mathscr{E}_{cell} = -\{\mathscr{E}^{oxid} - \mathscr{E}^{reduc}\}$. [f] This work. $\mathscr{E}_{cell}$ for this compound is highly typical of all dithiadiazole derivatives we have measured in CH_3CN solution, for which the average $\mathscr{E}_{cell} = -1.43 \pm 0.06$ V. [g] Reference 6d; from the difference in cathodic peak potentials, since the "reduction" process is highly irreversible. [h] Reference 6d; from two fully reversible electrochemical processes. [i] Reference 21, which reports the difference in the cathodic peak potentials. The average of the cathodic and anodic peak potentials gives an apparent $\epsilon_{cell} = -0.48$ V. [j] Reference 8a; ref 8b reports −0.38 V for this value. [k] Reference 8a; ref 8c reports −0.54 V for this value.

With these points in mind we recognize that **3**, **6**, $\mathbf{7}^-$, and $\mathbf{8}^+$ all have effective $\mathscr{E}_{cell}$ values of around −4 V in the gas phase and around −0.5 V in CH_3CN, whereas **1** has a gas phase $\mathscr{E}_{cell}$ of −6.5 V and in solution −1.5 V. Thus both solution measurement and gas-phase estimates indicate that the disproportionation energies of **1** are higher than desirable. The calculations show that this is primarily due to a destabilization (more positive enthalpy of formation) of the cationic form of **1, R = H** compared to $\mathbf{2}^+$ and $\mathbf{3}^+$. (Comparisons with **7** and **8** are complicated by differences in charge.) This is readily attributed to the high effective electronegativity of the nitrogen-containing rings, a feature which has been previously recognized.[3b]

Within the series of **1** reported here the most significant lowering of $\mathscr{E}_{cell}$ occurs (a) with the dimethylamino substituent and (b) by replacing sulfur with selenium. The magnitude of both effects is similar, suggesting that they should be combined (i.e. in **1, R = Me$_2$N, E = Se**). The synthesis of other amino-substituted dithia- and diselenadiazoles, including heterocyclic examples, would seem to be warranted. We note also that the magnitude of effects (a) and (b) is identical in both solvents. If they were caused largely by differential solvation, one would expect the variation in $\mathscr{E}_{cell}$ to be solvent dependent. In this connection it is worth noting that **4, E = Se**[2m] and **5, E = Se**[21] are intrinsic semiconductors, whereas the corresponding isostructural sulfur compounds are insulators. We believe that a more favorable disproportionation energy for the selenium-containing rings is one contributing factor to the higher intrinsic conductivity of these neutral π-radical materials.

Conclusions

The results from both the solution and gas-phase analysis is that the disproportionation energies of **1** are higher than

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desirable, and this may be one of the chief limitations in achieving a metallic state despite their other advantages. The calculations suggest that the chief contributor to these high energies is the cation, a consequence of the electronegative elements in the ring. Replacement of S by Se is predicted to favor a conducting state, and strongly electron-donating substituents such as amino groups may favor conduction. Multifunctional dithia- and diselenadiazoles have within experimental error the same electrochemical properties as similar monofunctional compounds. There is no electronic communication through the π-system of the benzenoid backbone in such bifunctional systems. Structural advantages accruing from such designs, which aid conduction by maximizing interstack contacts and enhancing the stacking geometry, may be pursued independently of the intrinsic disproportion energies, which we have shown to be identical to those of the monofunctional compounds. Finally, the remarkable result that selenium-for-sulfur replacement has no effect on the oxidation potentials is important to recent attempts to form partially oxidized derivatives of **1**. Such oxidations can be carried out with the same oxidizing agents irrespective of the choice of chalcogen in the parent radicals.

Experimental Section

The compounds investigated in this work are listed in the data tables, with literature references to their preparation and, in most cases, structural characterization. They were either obtained in the cation form by dissolving PF_6^- or SbF_6^- salts in CH_3CN or as the free radicals by dissolving the stable dimers in either CH_2Cl_2 or CH_3CN. Purification of the dimers was achieved by vacuum sublimation. Less volatile samples were sublimed in a three-zone tube furnace under static or dynamic vacuum using Pyrex sublimation tubes.

Cyclic voltammetry (scan rates $\nu = 20-5000$ mV s^{-1}), phase-sensitive alternating current experiments ($\omega = 610$ Hz, $\nu = 10$ mV s^{-1}), and coulometry were carried out with a PAR 173 potentiostat in combination with a PAR 175 programmer and EGG 9209 lock-in amplifier and recorded on a Houston Graphics 2000 XY plotter and a HP 181 storage oscilloscope or a Perkin Elmer strip chart recorder. For the voltammetric experiments the vacuum-tight all glass cell was employed which has been described previously.[14] The cell was charged with electrolyte ($N^nBu_4PF_6$), and the solvent, dry degassed CH_3CN or CH_2Cl_2, was transferred on a vacuum line. Samples and ferrocene as an internal reference were added to the cell using break-seal techniques. The ferricenium/ferrocene couple is observed in this system at +0.38 (CH_3CN) and +0.48 (CH_2Cl_2) V vs SCE at 25 °C.

For coulometric work an adaptation of the cell design has been utilized where movement of compound from the counter electrode to the working electrode has been restricted by a porous frit. The counter electrode compartment can be closed off completely by a Rotaflo-valve to allow for solute transfer to the working electrode compartment only. The working electrode was made from a 52 mesh platinum gauze with the dimensions 25 × 12.5 mm (250 mg), rolled into a cylindrical shape to fit into the cell. During the reduction of **4a**$^{2+}$(CH_3CN solution) to **4a**(solid) the experiment was halted after 1.70 equiv of charge had passed. The remaining 0.30 equiv required for a two-electron transfer are readily accounted for by a small amount of the starting salt coating the walls of the vessel, by inefficiencies attributable to the crystallization of product on the working electrode and by halting before T_∞ was reached. Similarly the reduction of **4b**$^{2+}$ was halted after 1.76 equiv of charge had passed.

The electronic structure calculations were carried out with the HyperChem package[23] following the procedure outlined in ref 4. For each of the compounds listed in Table 4, the geometry was optimized without symmetry constraints in MNDO in all three ionization states, i.e., the appropriate radical form, the radical less one electron, and the radical plus one electron. Calculated enthalpies of formation for each equilibrium geometry are tabulated, and the disproportionation energy and equivalent cell potentials calculated as indicated in Table 4.[24]

Acknowledgment. We thank Prof. R. T. Oakley for supplying pure samples of several of the compounds and NSERC (Canada) and the University of Lethbridge Research Fund for financial support. K.H.M. acknowledges receipt of a fellowship from the Alexander von Humboldt Foundation (Germany).

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[23] HyperChem Release 3 for Windows; Autodesk, Inc., 2320 Marinship Way, Sausalito, CA 94965, U.S.A., 1993.

[24] HyperChem has implemented MNDO along with several other semiempirical methods, but has rewritten the original FORTRAN code in C and C^{++}. These calculations are therefore not directly comparable to those from other popular packages containing MNDO. In order to facilitate comparisons, we are providing MOPAC-style Z-matrix files of the minimized geometries. These may be obtained from the corresponding author by E-Mail as file "DISPRO94.TXT".

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