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The preparation of, and electrochemical studies on, some substituted aryl dithiadiazolylium salts and dithiadiazolyl radicals

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Abstract—A series of aryl-substituted 1,2,3,5-dithiadiazolylium cations (**I**) and 1,3,2,4-dithiadiazolylium cations (**II**) were prepared as their hexafluoroarsenate(V) salts using standard methods. Electrochemical studies on **I** and **II** showed reversible one-electron reductions. The half-wave reduction potentials for a series of *meta*-substituted derivatives of both **I** and **II** exhibited a linear free energy relationship with the Hammett parameter, σ_m. The small value of the reaction constant, ρ, for both *meta* and *para*-derivatives indicates that electronic effects are small and in the case of the *ortho*-derivatives of **II**, steric effects dominate the redox process. Reduction of the 1,2,3,5-dithiadiazolylium cations, as their chloride salts, yielded the corresponding dithiadiazolyl radicals (**III**). © 1997 Elsevier Science Ltd

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Synthetic routes to simple derivatives of both the 1,2,3,5-dithiadiazolylium cation, **I**, and the 1,3,2,4-dithiadiazolylium cation **II** are now well-developed, and their chemistries have received some attention [1]. For instance, reduction of these cations leads to the formation of the corresponding radicals **III** and **IV**, respectively [1]. Although a few derivatives of type **IV** have been prepared and characterised in the solid state [2–3], they readily rearrange both in solution [4] and in the solid state [5] to the thermodynamically more stable isomer, **III**. The chemistry of **III** has also been studied [1]. Recently derivatives of type **III** have been utilised as molecular building blocks in the construction of molecular conductors [6] and molecular magnets [7]. In turn, this has led us to investigate the effect of substituents on the structural and electronic properties of these radicals in order that they can be modified in a controlled and well-defined manner. Recently we reported the preparation of two series of *para*-substituted derivatives of both types **I** and **II** and found a linear-free energy relationship between the redox behaviour of the heterocyclic ring and the Hammett parameters, σ_p [8]. In order to extrapolate these results further we have prepared, and carried out electrochemical investigations on, both *ortho*- and *meta*-substituted derivatives. We now report the results of these experiments.

RESULTS AND DISCUSSION

Syntheses

Simple aryl derivatives of **I**, as the chloride salt are typically prepared [8] by reaction of the parent nitrile with $Li[N(SiMe_3)_2]$, followed by condensation with SCl_2. Their metatheses with $AgAsF_6$ yield the hexafluoroarsenate(V) salts which are more amenable to electrochemical study because of their enhanced solubility [8]. Six novel *meta*-substituted derivatives were prepared by this method with recovered yields in the range 82–95%. Yields and micro-analytical data for these compounds are given in Table 1. In comparison, we found that this synthetic methodology is not generally applicable to the *ortho*-derivatives of

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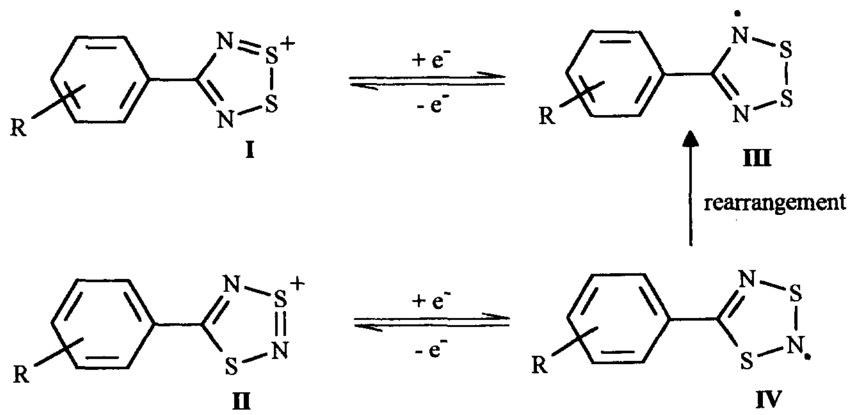

I; Attempts to prepare $[o\text{-ClC}_6\text{H}_4\text{CNSSN}]\text{Cl}$, $[o\text{-BrC}_6\text{H}_4\text{CNSSN}]\text{Cl}$ and $[o\text{-MeC}_6\text{H}_4\text{CNSSN}]\text{Cl}$ were unsuccessful, and yielded only the parent nitrile as the organic component. We were only able to obtain $[o\text{-FC}_6\text{H}_4\text{CNSSN}]\text{Cl}$ by this synthetic route (61%). Although the reaction mechanism is presently unclear, we believe that a key step must be nucleophilic attack of $[\text{N(SiMe}_3)_2]^-$ anion at C. The presence of a sterically demanding *ortho*-substituent hinders close approach of the nucleophile and inhibits the consequent addition reaction.† Reduction of derivatives of **I**, as their chloride salts, produced the corresponding radicals, **III**. Yields and micro-analytical data for these compounds are also given in Table 1.

In comparison, the cycloaddition reaction of $[\text{SNS}][\text{AsF}_6]$ with simple aromatic nitriles with both *ortho*- and *meta*-substituents proved facile. Yields (70–91%) and micro-analytical data for these compounds are given in Table 1. In addition to these new compounds, $[\text{PhCNSSN}][\text{AsF}_6]$, $[\text{PhCNSNS}][\text{AsF}_6]$ and $[m\text{-NCC}_6\text{H}_4\text{CNSSN}]_2$ were prepared according to the literature methods [9–11] and used in the following electrochemical studies.

Electrochemical studies of meta-*substituted derivatives*

The *meta*-substituted derivatives of **I** all exhibit quasi-reversible one-electron reductions, similar to the parent phenyl compound [8]. This is entirely consistent with a common electrochemical process, i.e. the one-electron reduction of **I** to form **III**. The range of half-peak reduction potentials, $E_{\text{pc}/2}$ for these compounds (Table 2) ranged from 645 to 590(±5) mV *vs* S.S.C.E. Equation 1 is derived [12] by combining the equations $\Delta G = -nEF$ and $\Delta G = -2.303RT\sigma 1\rho$. It relates the reduction potential, E, to the Hammett parameter, σ, a reaction constant, ρ, which reflects the susceptibility of the electroactive species to electronic effects, and the reduction potential of the unsubstituted (phenyl) derivative E_{H} :-

$$E = E_{\text{H}} + \sigma\rho \qquad (1)$$

A plot of the reduction potential, $E_{\text{pc}/2}$, for **I** *vs* the corresponding Hammett parameters for *meta*-substituents, σ_{m}, is shown in Fig. 1 and illustrates an excellent linear free energy relationship [$\rho = +0.1$ with a goodness of fit of 0.97]. Similar electrochemical investigations into *meta*-derivatives of the reduced product, **III**, showed, within error, identical $E_{\text{pc}/2}$ values (Table 2) to the derivatives of **I** ($\rho = +0.1$ with a goodness of fit = 0.99). These results indicate that the differences in the bulk solutions of the salt, **I**, and the corresponding radical, **III**, have a negligible effect on the redox couple and that both cations and radicals behave similarly in solution, i.e. solution interactions

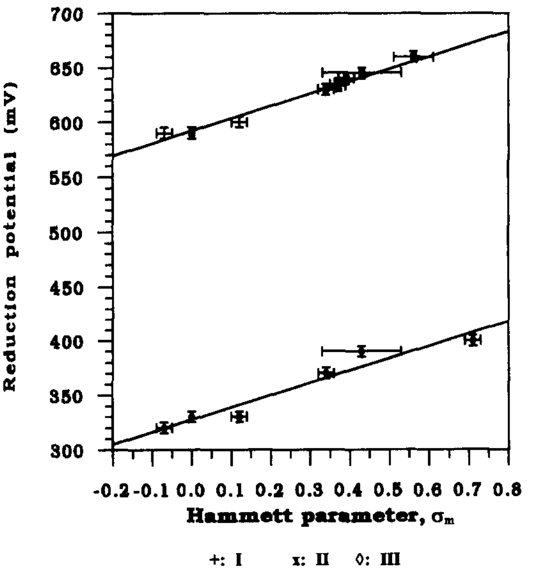

Fig. 1. Plot of the half-wave reduction potential, $E_{\text{pc}/2}$, as a function of the Hammett parameter, σ_{m} for derivatives of **I**, **II** and **III**.

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† It is not clear, however, why only one ortho-substituent should hinder reaction since a second face is still open to the nucleophile. We are presently carrying out further studies to characterise the nature of these intermediates in order to probe the mechanistic pathway in more detail.

Table 1. Yields and micro-analytical data for novel derivatives of **I**, **II** and **III**; theoretical values are given in parentheses

Compound	Colour	Yield (%)	C (%)	H (%)	N (%)	M.p. (°C)
$[m\text{-}CF_3C_6H_4\overline{CNSSN}]Cl$	bright yellow	87	34.20	1.56	10.12	
			(33.75)	(1.42)	(9.84)	
$[m\text{-}BrC_6H_4\overline{CNSSN}]Cl$	yellow	82	27.87	1.35	9.66	
			(28.44)	(1.36)	(9.48)	
$[m\text{-}ClC_6H_4\overline{CNSSN}]Cl$	yellow-orange	83	32.88	1.46	11.00	
			(33.48)	(1.61)	(11.16)	
$[m\text{-}FC_6H_4\overline{CNSSN}]Cl$	orange	82	35.65	1.93	11.01	
			(35.82)	(1.72)	(11.94)	
$[m\text{-}MeC_6H_4\overline{CNSSN}]Cl$	bright yellow	88	42.03	3.50	12.56	
			(41.64)	(3.06)	(12.14)	
$[m\text{-}MeOC_6H_4\overline{CNSSN}]Cl$	red	95	37.98	2.43	11.01	
			(38.94)	(2.86)	(11.36)	
$[m\text{-}CF_3C_6H_4\overline{CNSSN}][AsF_6]$	cream	82	22.01	1.01	6.90	
			(21.93)	(0.92)	(6.39)	
$[m\text{-}BrC_6H_4\overline{CNSSN}][AsF_6]$	orange-red	95	18.89	1.01	6.20	
			(18.72)	(0.90)	(6.24)	
$[m\text{-}MeC_6H_4\overline{CNSSN}][AsF_6]$	bright orange	80	25.20	1.90	7.39	
			(25.01)	(1.84)	(7.29)	
$[m\text{-}MeOC_6H_4\overline{CNSSN}][AsF_6]$	burgundy	89	24.30	1.57	6.83	
			(24.01)	(1.76)	(7.00)	
$[m\text{-}CF_3C_6H_4\overline{CNSSN}]_2$	lustrous bronze	68	39.01	1.70	11.28	82
			(38.55)	(1.62)	(11.24)	
$[m\text{-}BrC_6H_4\overline{CNSSN}]_2$	lustrous green	42	32.00	1.47	10.57	129
			(32.32)	(1.55)	(10.77)	
$[m\text{-}ClC_6H_4\overline{CNSSN}]_2$	red-green dichroic	64	39.45	1.90	12.59	117
			(38.98)	(1.87)	(12.99)	
$[m\text{-}FC_6H_4\overline{CNSSN}]_2$	red-green dichroic	68	41.76	2.00	13.94	128
			(42.19)	(2.02)	(14.06)	
$[m\text{-}O_2NC_6H_4\overline{CNSNS}][AsF_6]$	cream	89	20.68	0.87	10.34	
			(20.25)	(0.97)	(10.12)	
$[m\text{-}CF_3C_6H_4\overline{CNSNS}][AsF_6]$	cream	78	21.58	0.98	6.43	
			(21.93)	(0.92)	(6.39)	
$[m\text{-}MeC_6H_4\overline{CNSNS}][AsF_6]$	yellow	75	25.35	1.90	7.12	
			(25.01)	(1.84)	(7.29)	
$[m\text{-}MeOC_6H_4\overline{CNSNS}][AsF_6]$	tangerine	83	24.13	1.64	7.20	
			(24.01)	(1.76)	(7.00)	
$[o\text{-}FC_6H_4\overline{CNSSN}]Cl$	yellow	61	36.10	1.98	12.01	
			(35.88)	(1.72)	(11.94)	
$[o\text{-}FC_6H_4\overline{CNSSN}]_2$	red-green dichroic	45	42.90	2.05	14.50	
			(42.19)	(2.02)	(14.06)	
$[o\text{-}O_2NC_6H_4\overline{CNSNS}][AsF_6]$	white	82	20.68	1.04	10.50	
			(20.25)	(0.97)	(10.12)	
$[o\text{-}CH_3C_6H_4\overline{CNSNS}][AsF_6]$	yellow	77	21.50	1.01	6.90	
			(21.93)	(0.92)	(6.39)	
$[o\text{-}BrC_6H_4\overline{CNSNS}][AsF_6]$	yellow	76	18.90	0.70	6.70	
			(18.72)	(0.90)	(6.24)	
$[o\text{-}ClC_6H_4\overline{CNSNS}][AsF_6]$	yellow	75	20.90	0.80	6.76	
			(20.78)	(1.00)	(6.93)	
$[o\text{-}FC_6H_4\overline{CNSNS}][AsF_6]$	yellow	71	21.55	1.01	7.01	
			(21.66)	(1.04)	(7.22)	
$[o\text{-}MeC_6H_4\overline{CNSNS}][AsF_6]$	bright yellow	70	25.34	1.90	7.56	
			(25.01)	(1.84)	(7.29)	
$[o\text{-}MeOC_6H_4\overline{CNSNS}][AsF_6]$	bright orange	83	23.78	1.87	7.20	
			(24.01)	(1.76))	(7.00)	
$[o\text{-}EtOC_6H_4\overline{CNSNS}][AsF_6]$	mandarin	91	26.34	2.34	6.92	
			(26.09)	(2.19)	(6.76)	

Table 2. Half-wave reduction potentials for derivatives of **I**, **II** and **III** and the associated Hammett parameters, σ_m for meta-substituents

X	$E_{pc/2}$ [m-$XC_6H_4\overline{CNSSN}$][AsF_6]	$E_{pc/2}$ [m-$XC_6H_4\overline{CNSNS}$]	$E_{pc/2}$ [m-$XC_6H_4\overline{CNSNS}$][AsF_6]	σ_m [20]	$E_{pc/2}$ [o-$XC_6H_4\overline{CNSSN}$]	$E_{pc/2}$ [o-$XC_6H_4\overline{CNSNS}$][AsF_6]
NO_2			400	0.71±0.02		390
CN		660		0.56±0.05		
CF_3	645	645	390	0.43±0.1		403
Br		640		0.39±0.02		325
Cl	633	635		0.37±0.02		320
F		630	370	0.34±0.02	610	310
MeO	600		330	0.12±0.02		330
H	590	590	330	0.00	590	330
Me	590		320	−0.07±0.02		158
EtO						163

have approximately the same effect on the electronic environment of both cationic and radical ring systems and this is entirely consistent with them existing as monomeric species in the bulk solution. Although numerous crystallographic studies [1] have shown that the vast majority of derivatives of **III** dimerise in the solid state, ESR studies have shown that dissociation into discrete monomers is essentially complete at room temperature [13].

The *meta*-substituted derivatives of **II** also exhibit similar quasi-reversible electrochemical characteristics to **I** and **III**, although the reduction was in the range 320–400(±5) mV *vs* S.S.C.E. (Table 2). These derivatives also exhibit a linear free energy relationship (Fig. 2) with a reaction constant of 0.1 (goodness of fit of 0.94). The difference in reduction potentials is directly related to the energy of the LUMO of the parent cation, and theoretical calculations [1] have shown that **I** is more easily reduced than **II**. Derivatives of **IV** are susceptible to rearrangement [4–5] (either thermal or photochemical) and electrochemical studies on these derivatives were not carried out.

Comparison of substituent position on redox behaviour

The redox behaviour of the *para*-substituted phenyl derivatives of types **I** and **III** have been reported previously [8]. Both *meta*- and *para*-derivatives exhibit similar electrochemical behaviour in that linear free energy relationships exist between the Hammett parameters for the aryl substituents and the reduction potential, $E_{pc/2}$. The positive value of the reaction constant, ρ, indicates that the stronger the electron withdrawing ability of the substituent group, the more energetically favourable the reduction process is. This is entirely consistent with a reduction process in which the additional unpaired electron is stabilised by the presence of electron-withdrawing functionalities. The magnitude of ρ is the same, within experimental error, for both *meta*- and *para*-derivatives, although the magnitude of ρ is an order of magnitude less than that found for the ionisation of *meta*- and *para*-substituted benzoic acids (where $\rho = 1$ under standard conditions [14]). This is consistent with MO calculations which indicate that the reduction process involves the filling of an unoccupied orbital based entirely on the $\overline{CNSSN}$ ring and which, to a first order approximation, is unaffected by variation of substituent [8]. Although both *meta*- and *para*-derivatives have similar values of ρ, those *para*-compounds which can donate electrons through the mesomeric effect (e.g. F and MeO) have lower $E_{pc/2}$ values than the corresponding *meta* derivatives in which this process cannot occur. This phenomenon is, of course, accounted for in the different values of the Hammett parameters for *meta* and *para* substituents, σ_m and σ_p, respectively.

Electrochemical studies of ortho-*substituted derivatives*

Hammett parameters can be used to predict electronic influences on chemical processes but do not account for steric or through-space interactions. Therefore, it has proved difficult to predict [15] reliable Hammett parameters for *ortho* substituents because of steric effects which often contribute more strongly than the electronic effects. For example, σ_o values for the pK_a values of substituted phenols and substituted benzoic acids differ markedly due to the differing steric effects [15]. In this work we have already seen that the electronic effect of the substituents on the redox couple is small ($\rho \sim 0.1$ for both *meta* and *para* derivatives) and therefore we might anticipate steric effects to predominate in the *ortho*-derivatives.

Only [o-FC_6H_4CNSSN] was studied as an example of **III** due to the synthetic problems previously described. This derivative showed a quasi-reversible reduction process typical of **I** and **III**. In comparison, nine *ortho*-substituted derivatives of **II** were prepared and studied by electrochemistry. All revealed quasi-reversible behaviour akin to both *meta* and *para* derivatives. The $E_{pc/2}$ values were in the region 157–390(±5) mV *vs* S.S.C.E. (Table 2). In agreement with our predictions, we observe a greatly enhanced spread of $E_{pc/2}$ values consistent with electronic or steric through-space (rather than through bond) control of the redox process; *meta*- and *para*-derivatives exhibit a spread of only some 75 mV whereas a similar set of *ortho* derivatives produce a spread of *ca* 250 mV. The most notable deviations are the methoxy- and ethoxy-derivatives which prove exceptionally difficult to reduce. This through-space interaction has been noted previously in the ESR spectra of fluorinated derivatives of **III** in which hyperfine coupling is observed to *ortho*-fluorines but not to *meta*- or *para*-fluorine atoms [16].

EXPERIMENTAL

General procedures

All reactions and manipulations were carried out using standard vacuum line and analytical techniques (IR, DSC, mass spectra) described elsewhere [8]. Cyclic voltammetry experiments were carried out using experimental procedures and conditions described previously [8].

Starting materials

All solid nitriles were sublimed *in vacuo* before use. Other nitriles, Li[N($SiMe_3$)$_2$], SCl_2 and $AgAsF_6$ (Aldrich) were used without further purification. [PhCNSSN][AsF_6], [PhCNSNS][AsF_6], [*m*-NCC_6H_4CNSSN]$_2$, [PhCNSSN]$_2$ and [SNS][AsF_6], were prepared according to the literature methods [9,11,17,18]. Yields and microanalytical data for all new compounds are given in Table 1. Details of IR and mass spectra are given in Tables 3 and 4.

Syntheses of [ArCNSSN]Cl

In a typical experiment, ArCN (0.010 mol) and Li[N($SiMe_3$)$_2$] (0.010 mol) were placed in a 2-necked RB flask and Et_2O (*ca* 60 cm^3) added. The reaction was stirred for 3 h at room temperature and then cooled to 0°C. A slight excess of SCl_2 (0.022 mol) was added slowly to yield an instantaneous coloured precipitate. The mixture was warmed to room temperature and stirred for 5 h followed by solvent removal *in vacuo*. The crude product was transferred to a sealed soxhlet extractor [19] and exhaustively extracted with liquid SO_2 to remove LiCl. The product was washed with CH_2Cl_2 (10 cm^3) and dried *in vacuo*.

Syntheses of [ArCNSSN][AsF_6]

In a typical experiment, [ArCNSSN]Cl (0.001 mol) and $AgAsF_6$ (0.297 g, 0.001 mol) were placed in a two-limbed reaction vessel [9] and liquid SO_2 (*ca* 8 cm^3) condensed in. The reaction mixture was stirred for 18 h at room temperature, to yield a coloured solution over a white precipitate (AgCl). The solution was filtered off and the white precipitate washed with back-condensed SO_2 until the washings were colourless. The solvent was removed *in vacuo* to yield [ArCNSSN][AsF_6] as a microcrystalline solid.

Syntheses of [ArCNSSN]$_2$

In a typical experiment, [ArCNSSN]Cl (0.02 mol) and an excess of Zn/Cu couple (*ca* 0.01 mol) were placed in a Schlenk tube and THF (30 cm^3) added. The reaction mixture was stirred at room temperature for 5 h during which time the reaction mixture became progressively darker. The solvent was removed *in vacuo* to yield a dark solid which was purified by vacuum sublimation (10^{-1}–10^{-2} torr, temperatures in the region 80–140°C).

Syntheses of [ArCNSNS][AsF_6]

In a typical reaction ArCN (0.001 mol) and [SNS][AsF_6] (0.267 g, 0.001 mol) were placed in a two-limbed reaction vessel [9] and SO_2 (*ca* 8 cm^3) condensed in. The reaction mixture was stirred at room temperature for 18 h and the volume of solvent reduced to *ca* 0.5 cm^3. CH_2Cl_2 (*ca* 8 cm^3) was then added to precipitate the product which was filtered off, washed with further aliquots of CH_2Cl_2 (2 × 8 ml) and dried *in vacuo*.

Table 3. IR data [ν_{max}/cm^{-1}] for selected derivatives of **I**, **II** and **III**

Meta derivatives of **I**	
$[m\text{-}CF_3C_6H_4\overline{CNSSN}]Cl$	1610 m, 1594 vw, 1461 s, 1397 s, 1377 m, 1324 s, 1312 s, 1294 s, 1190 s, 1172 s, 1123 s, 1096 m, 1075 s, 1000 vw, 953 s, 924 w, 913 m, 893 s, 850 s, 814 s, 786 vw, 722 s, 696 s, 690 m, 647 w, 620 w, 547 s, 528 m
$[m\text{-}BrC_6H_4\overline{CNSSN}]Cl$	1564 m, 1464 s, 1428 m, 1379 s, 1295 w, 1275 w, 1212 w, 1156 m, 1086 w, 1068 m, 994 m, 938 s, 896 s, 890 s, 847 s, 806 s, 715 vs, 672 m, 644 vw, 547 s, 518 m, 434 w
$[m\text{-}ClC_6H_4\overline{CNSSN}]Cl$	1573 m, 1464 s, 1436 m, 1380 s, 1313 w, 1298 w, 1275 w, 1212 w, 1160 m, 1138 w, 1092 m, 1072 m, 997 w, 948 s, 896 s, 848 s, 804 s, 742 s, 717 vs, 674 m, 548 s, 526 m
$[m\text{-}FC_6H_4\overline{CNSSN}]Cl$	1676 m, 1587 s, 1493 m, 1453 s, 1387 s, 1312 m, 1300 m, 1281 w, 1227 m, 1138 m, 1124 m, 1076 w, 1002 w, 976 s, 900 s, 856 m, 822 s, 801 s, 772 w, 723 vs, 674 m, 549 m, 526 m, 464 w
$[m\text{-}MeC_6H_4\overline{CNSSN}]Cl$	1584 w, 1459 s, 1379 vs, 1307 m, 1221 m, 1168 vw, 1136 m, 1090 w, 1048 vw, 999 vw, 956 w, 926 w, 892 s, 851 s, 806 m, 717 vs, 684 w, 617 vw, 546 s, 526 m
$[m\text{-}MeOC_6H_4\overline{CNSSN}]Cl$	1600 m, 1579 m, 1490 m, 1461 vs, 1375 s, 1347 s, 1288 m, 1265 w, 1252 m, 1238 m, 1200 w, 1181 w, 1156 w, 1110 s, 1085 w, 1040 m, 954 m, 940 m, 886 w, 858 w, 810 w, 800 w, 755 vs, 732 s, 704 s, 682 m, 545 vw, 519 w, 443 s
$[m\text{-}BrC_6H_4\overline{CNSSN}][AsF_6]$	1684 m, 1595 w, 1570 m, 1478 m (sh), 1464 s, 1433 s, 1384 vs, 1303 w, 1278 m, 1168 m, 1090 w, 1073 m, 996 w, 957 w, 930 m, 914 m, 894 m, 850 m, 799 s, 704 vs (br), 673 s, 557 m, 516 w
$[m\text{-}MeC_6H_4\overline{CNSSN}][AsF_6]$	1665w (br), 1604 w, 1587 m, 1462 vs (br) 1378 vs (br), 1290 m, 1228 w, 1143 w, 1092 w, 933 m, 922 s, 858 vw, 800 s, 703 vs (br), 560 m, 517 vw
$[m\text{-}MeOC_6H_4\overline{CNSSN}][AsF_6]$	1670 w (br), 1602 m, 1578 s, 1510 w, 1493 m, 1460 vs (br), 1378 vs, 1297 s, 1256 s, 1175 vw, 1136 m, 1092 w, 1036 vs, 992 vw, 965 w, 921 m, 898 w, 883 m, 856 w, 805 s, 788 m, 706 vs (br), 673 vs, 554 s, 478 vw
Meta derivatives of **III**	
$[m\text{-}CF_3C_6H_4\overline{CNSSN}]_2$	1612 vw, 1463 s, 1376 s, 1320 s, 1287 s, 1164 m, 1137 s, 1115 s, 1091 m, 1071 m, 930 m, 920 m, 835 w, 814 m, 788 m, 776 m, 722 vw, 694 m, 685 s, 664 vw, 648 w, 600 vw, 518 m, 448 vw, 420 vw
$[m\text{-}BrC_6H_4\overline{CNSSN}]_2$	1700 w, 1561 w, 1467 m, 1427 m, 1365 m, 1280 w, 1242 w, 1160 w, 1142 w, 1081 w, 1070 m, 994 w, 915 m, 898 m, 837 m, 801 s, 790 s, 777 s, 710 s, 691 s, 648 w, 512 s, 502 m, 426 w, 400 w
$[m\text{-}ClC_6H_4\overline{CNSSN}]_2$	1594 vw 1573 w, 1463 s, 1433 m, 1366 s (br), 1297 vw, 1275 w, 1230 w, 1163 w, 1143 m, 1088 w, 1074 w, 998 vw, 928 m, 884 m, 833 m, 803 m (sh), 788 s, 777 vs, 740 s, 689 vs, 519 m, 502 m, 469 vw, 429 w
$[m\text{-}FC_6H_4\overline{CNSSN}]_2$	1610 w, 1587 m, 1488 m, 1450 s, 1366 s, 1277 m, 1235 w, 1211 m, 1158 m, 1107 s, 1077 m, 961 s, 876 m, 837 m, 820 s, 793 vs, 692 s, 660 w, 542 m, 526 w, 512 s, 459 w, 426 w
Ortho derivatives of **I**	
$[o\text{-}FC_6H_4\overline{CNSSN}]Cl$	1677 w, 1610 s, 1600 m (sh), 1493 m, 1457 s, 1394 s, 1383 m, 1306 s, 1274 m (sh), 1234 s, 1162 m, 1141 m, 1102 m, 1032 w, 934 w, 900 s, 846 s, 813 s, 773 vs, 755 m, 741 s, 674 m, 684 m, 640 w, 562 s, 530 s
Ortho derivatives of **III**	
$[o\text{-}FC_6H_4\overline{CNSSN}]_2$	1608 m, 1579 w, 1491 m, 1458 s, 1369 s, 1274 m, 1223 m, 1160 w, 1141 m, 1095 m, 1034 m, 949 vw, 908 w, 864 vw, 838 m, 804 s, 777 vs, 763 vs, 731 m, 652 m, 640 m (sh), 550 m, 511 m, 488 vw, 416 w
Ortho derivatives of **II**	
$[o\text{-}CF_3C_6H_4\overline{CNSNS}][AsF_6]$	1676 vw, 1597 m, 1580 m, 1419 m (sh), 1318 m, 1302 m (sh), 1160 w, 1121 s (br), 1067 m, 1041 m, 985 m, 908 w, 879 w, 803 s, 784 s, 704 vs (br), 662 m (sh), 639 m (sh), 598 m (sh), 589 m, 570 m, 452 s
$[o\text{-}BrC_6H_4\overline{CNSNS}][AsF_6]$	1734 w, 1646 vw (br), 1584 vw (br), 1559 s, 1308 w, 1292 w, 1276 m, 1213 vw, 1170 w, 1126 vw (sh), 1082 vw, 1059 w, 1029 s, 983 s, 915 m, 903 w, 794 s, 780 m, 771 s, 755 vw, 701 vs (br), 669 w (sh), 577 m, 484 vw, 451 vw (sh), 440 w, 428 vw (sh)
$[o\text{-}ClC_6H_4\overline{CNSNS}][AsF_6]$	1660 s, 1592 w (sh), 1133 m, 1059 s, 1035 w, 984 m (br), 717 w, 756 w, 72 vs (br), 630 m (sh), 575 m, 556 s, 490 w
$[o\text{-}FC_6H_4\overline{CNSNS}][AsF_6]$	1648 w, 1612 s (br), 1514 vw (sh), 1486 m, 1403 s, 1318 w, 1287 m, 1270 w, 1237 m, 1224 w, 1200 w, 1162 m, 1157 w, 1109 m, 1100 w (sh), 1028 vw (br), 990 s, 968 w, 923 m, 917 w, 898 m, 875 w, 860 vw (br), 815 m, 792 s, 779 s, 770 m (sh), 758 vw, 737 w (sh), 700 vs (br), 670 m (sh), 630 w, 585 w, 540 w, 524 vw (br), 456 w (br), 438 m, 400 vs
$[o\text{-}MeC_6H_4\overline{CNSNS}][AsF_6]$	1600 w, 1402 s, 1294 m, 1212 w, 1172 w, 1116 vw, 980 w, 911 vw, 806 m, 772 s, 760 w (sh), 692 vs (br), 636 m, 588 vw, 444 m (sh)
$[o\text{-}MeOC_6H_4\overline{CNSNS}][AsF_6]$	1560 w, 1462 vs, 1405 m, 1377 s, 1293 w, 1213 w (br), 1130 w (br), 1084 w, 980 w, 916 w, 806 m, 774 m, 758 m, 698 vs (br), 636 w, 584 w, 460 w, 443 w

Table 4. Mass spectral data [$m/z - EI^+$; (amu, %)] for selected derivatives of **III**

$[m\text{-}CF_3C_6H_4\overline{CNSSN}]_2$	$CF_3C_6H_4CNSSN$ (249, 61.6), $CF_3C_6H_4CNS$ (203, 29.7), $CF_3C_6H_4CN$ (171, 11.9), $CF_2C_6H_4CN$ (152, 14.0), $CF_3C_6H_4$ (145, 13.5), C_6H_4FCN (121, 13.5), S_2N (78, 100.0), SN (46, 23.0)
$[m\text{-}BrC_6H_4\overline{CNSSN}]_2$	$^{81}BrC_6H_4CNSSN$ (261, 33.0), $^{79}BrC_6H_4CNSSN$ (259, 34.9), $^{81}BrC_6H_4CNS$ (215, 11.6), $^{79}BrC_6H_4CNS$ (213, 11.7), $^{81}BrC_6H_4CN$ (183, 14.5), $^{79}BrC_6H_4CN$ (181, 14.9), C_6H_4CNS (134, 14.5), C_6H_4CNSSN (102, 38.4), S_2N (78, 100.0), SN (46, 29.3)
$[m\text{-}ClC_6H_4\overline{CNSSN}]_2$	$^{37}ClC_6H_4CNSSN$ (217, 11.5), $^{35}ClC_6H_4CNSSN$ (215, 30.5), $^{37}ClC_6H_4CNS$ (171, 7.0), $^{35}ClC_6H_4CNS$ (169, 21.1), $^{37}ClC_6H_4CN$ (139, 10.8), $^{35}ClC_6H_4CN$ (137, 31.1), C_6H_4CN (102, 22.4), S_2N (78, 100.0), SN (46, 30.4)
$[m\text{-}FC_6H_4\overline{CNSSN}]_2$	FC_6H_4CNSSN (199, 55.1), FC_6H_4CNS (153, 38.3), FC_6H_4CN (121, 48.8), FC_6H_4 (95, 18.5), S_2N (78, 100.0), S_2 (64, 32.6), SN (46, 8.0)

CONCLUSIONS

The standard synthetic routes to *meta*- and *para*-substituted phenyl-1,2,3,5-dithiadiazolylium salts are not generally applicable to *ortho*-substituted derivatives and this has been attributed to steric hindrance. Only *ortho* fluoro-derivatives of I have been prepared using this synthetic methodology. In comparison, the cycloaddition of [SNS][AsF_6] to aryl-nitriles with *ortho*-, *meta*- or *para*-substituents, produces the corresponding 1,3,2,4-dithiadiazolylium salts in high yield. An examination of the redox couple of *ortho*, *meta*- and *para*-substituted aryl dithiadiazolylium and dithiadiazolyl species indicate a common quasi-reversible redox process. The *meta*- (and *para*) derivatives exhibit a linear free energy relationship in which electron withdrawing substituents assist the reduction process and half-wave reduction potentials may be predicted for new derivatives using the appropriate value of σ for each substituent. In comparison no linear free energy relationship was observed for *ortho* derivatives due to through-space effects on the redox couple.

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