Electrochemical Studies of Some Dithiadiazolylium Cations; Evidence for the Dithiadiazolide Anion, [PhCNSSN]⁻†

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A series of *para*-substituted aryldithiadiazolylium salts [p-XC₆H₄CNSSN][Y] (X = H, Me, CF₃, MeO, MeS, NO₂, F, Cl, Br, CN or CNSSN⁺; Y = Cl or AsF₆) and [p-XC₆H₄CNSNS][AsF₆] (X = H, Me, CF₃, MeO, MeS, NO₂, F, Cl, Br or CNSNS⁺) has been prepared. An electrochemical study of both 1,2,3,5- and 1,3,2,4-dithiadiazolylium derivatives, as the hexafluoroarsenate(V) salts, showed reversible redox behaviour, forming the corresponding dithiadiazolyl radicals. The half-wave reduction potentials, $E_{\frac{1}{2}}$(red), for the two isomeric dithiadiazolylium cations showed linear free-energy relationships between $E_{\frac{1}{2}}$(red) and the Hammett value, σ_p, for the substituent group X; the σ_p values for CNSSN⁺ and CNSNS⁺ rings have been calculated at +0.537 ± 0.005 and +0.57 ± 0.02 respectively. A second reduction process was also observed for both 1,2,3,5- and 1,3,2,4-dithiadiazolylium cations, indicative of the formation of the dithiadiazolide anion, [p-XC₆H₄CNSSN]⁻; a preparative-scale reduction of (PhCNSSN)₂ using sodium amalgam and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) provided a yellow air-sensitive solid, [Na(18-crown-6)][PhCNSSN].

Recent studies of dithiadiazol-yl/-ylium species[1] have been primarily concerned with their potential applications as organic metals; the multi(dithiadiazolyl) radicals[2–4] and charge-transfer salts[5] are of particular interest. The molecular packing of these materials in the solid state, which is a key factor in the properties of such materials, appears to be particularly susceptible to the aryl/alkyl substituent, and variations in the functional group can also lead to important variations in structure. For example, (PhCNSSN)₂[6] shows a *cis*-antarafacial arrangement **I** of dithiadiazolyl rings, (MeCNSSN)₂[7] a twisted configuration **II**, whilst (m-NCC₆H₄CNSSN)₂[8] shows a *trans*-antarafacial arrangement of dithiadiazolyl rings **III**.

Such variations in the substituent group may also lead to variations in the redox potential of these dithiadiazol-yl/-ylium heterocycles (see below) and consequently the degree of charge transfer, which is highly influential in the formation of donor–acceptor salts.[9] We now describe the synthesis and characterisation of some simple *p*-substituted aryldithiadiazolylium derivatives in order to examine the substituent effects on the redox chemistries of these heterocyclic rings. The electrochemical behaviour of a series of both 1,2,3,5- and 1,3,2,4-dithiadiazolylium cations, as the hexafluoroarsenate(v) salts, is discussed and a Hammett correlation between the half-wave reduction potential, $E_{\frac{1}{2}}$(red), and σ_p is observed for both dithiadiazolylium ring systems. Cyclic voltammetry also shows evidence for the formation of a dithiadiazolide anion and we describe the synthesis and isolation of the first dithiadiazolide in the form [Na(18-crown-6)][PhCNSSN] where 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

Experimental

General Procedures.—All reactions and manipulations were carried out under an atmosphere of dry nitrogen and solvents were dried before use. Infrared spectra were recorded as Nujol

I

II

III
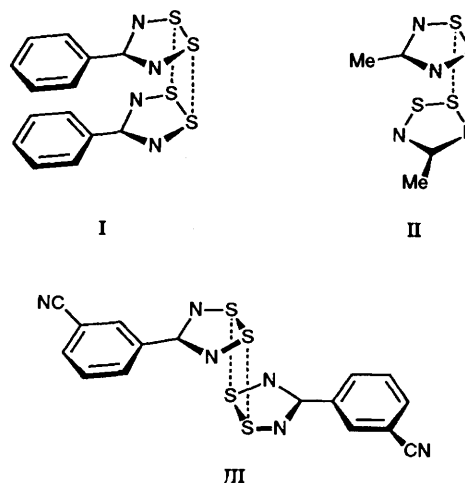
mulls between CsI or KBr plates using a Perkin-Elmer 577 or 457 grating spectrophotometer. Carbon, H and N analyses were carried out on a Carlo-Erba 1106 elemental analyser.

Cyclic voltammetry was typically carried out at −10 °C in a three-limbed vessel previously described,[10] using a Ag–Ag⁺ reference electrode, a potential-wave generator (type CV-1B; Bioanalytical Systems, W. Lafayette, IN) and a Linseis x-y chart recorder (type LY 17100). The temperature was regulated using a Haake C bath fitted with a F2 control unit. The Ag–Ag⁺ reference electrode (Fig. 1) is a modification by Dr. Z. V. Hauptman of his earlier design[10] and incorporates a silver electrode screwed onto a central rod. The side arm acts as a reservoir for excess of electrolyte solution such that the volume of electrolyte in the electrode may remain constant (any air-bubbles in the electrode may be removed by opening the tap). In this way the reproducibility of the electrode potential is improved by a factor of 10, from ±50 to ±5 mV. Since the electrode is completely filled with electrolyte solution (usually [NBu₄][BF₄] or [NBu₄][AsF₆]) and is separated from the
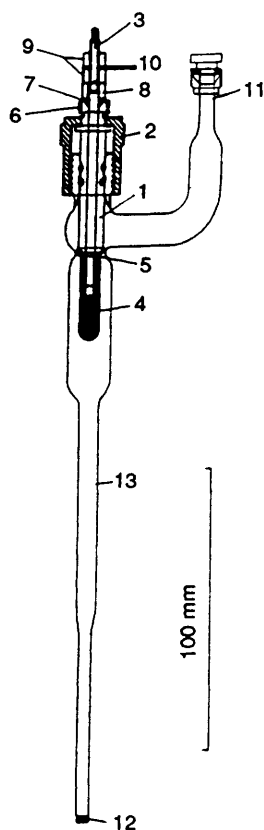

Fig. 1 The Ag–Ag$^+$ reference electrode: 1 = poly(tetrafluoroethylene) (ptfe) stem of J. Young greaseless tap; 2 = turning knob of J. Young greaseless tap; 3 = $\frac{1}{8}$ in outside diameter monel rod with 5BA thread at both ends; 4 = silver electrode screwed onto central rod; 5 = knife-edge machined on the flat edge of 4 to achieve a tight seal; 6 = brass ring around ptfe stem to prevent yielding through axial compression; 7 = O ring in conical groove machined in the top of the ptfe stem; 8 = washer; 9 = 5BA nuts; 10 = soldering eyelet; 11 = side arm of J. Young greaseless tap, fitted with a $\frac{1}{4}$ in Swagelok cap to form an air-tight reservoir for supporting electrolyte; 12 = Pyrex sinter, porosity grade 4; 13 = $\frac{1}{4}$ in outside diameter section for air-tight mounting via Swagelok fittings

electroactive species by a high-density Pyrex sinter, it can be used with pressurised solvent systems such as liquid SO_2. The $\frac{1}{4}$ in outside diameter glass tube facilitates the use of Swagelok fittings and provides an air-tight seal, suitable for an examination of air-sensitive materials. Since the electrode is not refilled between each experiment, its potential remains stable even over a period of 6 months to 1 year. The Ag–Ag$^+$ reference electrode was calibrated to the standard saturated calomel electrode (SCE) via a 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] salt bridge, before each experiment. Solutions (ca. 1 × 10^{-3} mol dm^{-3}) of the electroactive species were prepared in MeCN and 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] supporting electrolyte.

Starting Materials.—The salt [SNS][AsF$_6$] was prepared according to the literature method[11] with some amendments.[2d] The solid nitriles p-XC$_6$H$_4$CN (X = Me, CF$_3$, MeO, MeS, NO$_2$, F, Cl, Br or CN) (Aldrich) were sublimed *in vacuo* prior to use. Benzonitrile (Aldrich) was distilled onto molecular sieve and stored under nitrogen prior to use. The compounds Li[N(SiMe$_3$)$_2$] and AgAsF$_6$ (Aldrich) were used without further purification; p-[SNSNCC$_6$H$_4$CNSNS][AsF$_6$]$_2$,[2a] p-[NSSNCC$_6$H$_4$CNSSN]Cl$_2$,[4b] [PhCNSSN][AsF$_6$],[7] (PhCNSSN)$_2$,[12] p-[ClC$_6$H$_4$CNSSN][AsF$_6$],[7] [p-NCC$_6$H$_4$-CNSSN][AsF$_6$],[2d] [PhCNSNS][AsF$_6$][13,14] and [p-O$_2$NC$_6$H$_4$-

CNSNS][AsF$_6$][14] were prepared according to the literature methods.

Preparations.—[p-XC$_6$H$_4$CNSSN]Cl (X = H, Me, CF$_3$, MeO, MeS, NO$_2$, F, Cl, Br or CN). These compounds were typically made by an amended version[2d] of the literature method.[15] In a typical reaction, Li[N(SiMe$_3$)$_2$] (10 mmol) and p-XC$_6$H$_4$CN (10 mmol) were stirred in anhydrous diethyl ether (ca. 50 cm^3) for 12 h at room temperature to give a straw coloured solution. The ether solution was then added slowly to a slight excess of SCl$_2$ (25 mmol) to produce an immediate highly coloured precipitate. Stirring was continued for 5 h before drying *in vacuo*. The crude solid product was then transferred to a sealed extractor[16] and exhaustively extracted with liquid SO$_2$ to leave insoluble LiCl. The SO$_2$ was removed and the highly coloured product transferred to a two-limbed reaction vessel[5a] and washed repeatedly with CH$_2$Cl$_2$ (ca. 10 cm^3) by back condensation, before being dried *in vacuo*. Yields, analyses and colours are given in Table 1.

IR: (X = CF$_3$), ν_{max} 1520w, 1417w, 1405m, 1322s, 1250w(br), 1222w, 1170m, 1157m, 1140m, 1122s, 1110m, 1065s, 1012s, 985w, 920w, 890s, 860s, 845s, 770w, 755m, 750m, 698m, 690m, 680 (sh), 595m, 550m and 515w (br); (X = Br), 1680w (br), 1592m, 1390s, 1290w, 1180m, 1160m, 1070m, 1010s, 960w, 920w, 890s, 843s, 770w, 730s, 700m, 680s, 625w, 545s and 495m; (X = F), 1600s, 1515m (br), 1395s, 1300m, 1270w, 1240m, 1225m, 1165s, 1105vw, 1090w, 1040w, 1010w, 930m, 900s, 890s, 845s, 810m, 735s, 680m, 588m, 550m and 515m; (X = MeS), 1590s, 1438s, 1395s, 1180m, 1140m, 1117w, 1090m, 1005w, 970w, 930m, 882s, 832s, 728s, 680m, 550s and 500w; (X = Me), 1605m, 1400s, 1300vw, 1215w, 1200m, 1185w, 1160m, 1040m, 1024m, 925s, 900s, 845s, 825m, 724s, 685m, 548m, 525w and 490m; (X = MeO), 1605m, 1400s, 1300vw, 1215w, 1200m, 1185w, 1160m, 1040m, 1024m, 925s, 900s, 845s, 825m, 724s, 685m, 548m, 525w and 490m cm^{-1}.

[p-XC$_6$H$_4$CNSSN][AsF$_6$] (X = H, Me, CF$_3$, MeO, MeS, NO$_2$, F, Cl, Br or CN). In a typical reaction [p-XC$_6$H$_4$-CNSSN]Cl (1 mmol) and AgAsF$_6$ (1 mmol) were stirred in liquid SO$_2$ (ca. 7 cm^3) in one limb of a two-limbed reaction vessel[5a] for 18 h to give a coloured solution over a white precipitate (AgCl). After filtration, the white solid was washed with back-condensed SO$_2$ until the washings were colourless. The SO$_2$ was then removed and the filtrate dried *in vacuo*. Yields, analyses and colours are given in Table 1. The compound p-[NSSNCC$_6$H$_4$CNSSN][AsF$_6$]$_2$ was prepared in a similar manner.

IR: (X = CF$_3$), ν_{max} 1515w, 1447m, 1410m, 1320s, 1187s, 1122s, 1070s, 1020m, 986m, 970w, 917m, 852s, 804m, 695s (br), 670m, 634m, 590w, 443m and 400s; (X = Br), 1680w (br), 1590s, 1400s, 1310vw, 1290w, 1200w, 1182m, 1160m, 1114w, 1075m, 1012m, 962w, 940w, 922s, 840s, 835s, 730s, 700vs (br), 675 (sh), 560m, 498m and 397vs; (X = F), 1670m (br), 1602s, 1520w, 1402s, 1304m, 1260m, 1247s, 1197w, 1168s, 1165w, 1160s, 1112w, 1015w, 970vw, 960vw, 945vw, 927s, 849s, 825w, 810m, 740s, 730s, 695s (br), 675s, 592m, 560m, 519m, 400s (br) and 375m; (X = MeS), 1590s, 1415m, 1390s (br), 1198s, 1190 (sh), 1168m, 1094s, 1015m, 980w, 970w, 965w, 925m, 844s, 840m, 830m, 730s, 725m, 700s (br), 685 (sh), 675m, 560m, 502w, 495w, 400s and 390 (sh); (X = Me), 1735w (br), 1680m (br), 1606s, 1395s, 1300w(br), 1190s, 1163m, 1020w, 925s, 845m, 840m, 825s, 790w, 730 (sh), 703vs (br), 671s, 560m, 498w and 396vs; (X = MeO), 1680m, 1605s (br), 1582m, 1570m, 1520w, 1430m, 1400vs, 1370 (sh), 1335w, 1320m, 1309s, 1300w, 1278s, 1267m, 1177s, 1120m, 1020s, 952w, 930s, 840s, 818m, 810m, 790m, 742m, 700vs (br), 672s, 630w, 591m, 550m, 510m and 390vs (br) cm^{-1}.

[p-XC$_6$H$_4$CNSNS][AsF$_6$] (X = H, Me, CF$_3$, MeO, MeS, NO$_2$, F, Cl or Br). In a typical reaction p-XC$_6$H$_4$CN (2 mmol)

Table 1 Yields, analyses and colours for the dithiadiazolylium salts

X	Yield (%)	Colour	Found C	H	N	Required C	H	N
(a) [p-XC₆H₄CNSSN]Cl								
NO₂	65	Orange	32.00	1.55	16.00	32.15	1.55	16.05
CN	72	Orange	39.75	1.70	17.15	39.75	1.65	17.40
CF₃	58	Lemon-yellow	33.50	1.45	9.80	33.75	1.40	9.85
Br	60	Orange	29.00	1.50	9.50	28.45	1.35	9.50
Cl	75	Orange	33.45	1.65	11.30	33.45	1.60	11.15
F	63	Orange	35.80	1.70	11.35	35.85	1.90	11.20
H	77	Orange	38.70	2.40	12.45	38.80	2.30	12.95
MeS	60	Black-dark red	36.90	2.70	10.60	36.55	2.70	10.65
Me	55	Orange	40.90	3.00	12.00	41.65	3.05	12.15
MeO	67	Dark red	38.65	2.70	11.45	38.95	2.85	11.35
CNSSN⁺	69	Orange	27.35	1.15	15.90	28.00	1.15	16.35
(b) [p-XC₆H₄CNSSN][AsF₆]								
NO₂	84	Yellow	20.25	1.05	9.95	20.25	0.95	10.10
CN	92	Yellow	24.10	1.25	10.95	24.30	1.00	10.65
CF₃	83	Lemon-yellow	22.45	1.05	6.45	21.95	0.90	6.30
Br	80	Orange	18.50	1.00	6.10	18.70	0.90	6.25
Cl	83	Orange	20.65	1.05	7.00	20.80	1.00	6.95
F	84	Orange	21.55	1.05	7.15	21.65	1.05	7.20
H	93	Red-orange	22.70	1.40	7.70	22.70	1.35	7.55
MeS	86	Malachite green	22.80	1.60	6.55	23.10	1.70	6.75
Me	87	Red-orange	24.85	1.90	7.15	25.00	1.85	7.30
MeO	70	Purple	23.80	1.75	6.80	24.00	1.75	7.00
CNSSN⁺	82	Yellow	14.35	0.55	8.65	14.50	0.60	8.45
(c) [p-XC₆H₄CNSNS][AsF₆]								
NO₂	88	Off-white	20.35	1.05	10.00	20.25	0.95	10.10
CF₃	92	Peach	21.55	0.95	6.40	21.95	0.90	6.30
Br	80	Yellow	18.90	0.90	6.30	18.70	0.90	6.25
Cl	95	Yellow	20.45	1.00	6.95	20.80	1.00	6.95
F	96	Yellow	21.30	0.95	7.15	21.65	1.05	7.20
H	95	Lime-green	22.65	1.35	7.70	22.70	1.35	7.55
MeS	83	Red-black	23.40	1.90	6.75	23.10	1.70	6.75
Me	72	Lemon-yellow	24.75	1.80	7.20	25.00	1.85	7.30
MeO	65	Red	23.90	1.75	6.85	24.00	1.75	7.00
CNSNS⁺	92	Cream	14.95	0.55	8.25	14.50	0.60	8.45

and [SNS][AsF₆] (0.534 g, 2 mmol) were placed in one limb of a two-limbed vessel[5a] and SO_2 (ca. 7 cm³) condensed in. On warming to room temperature a highly coloured solution formed which was stirred for 5 h. The volume of solvent was reduced to less than 1 cm³ and CH_2Cl_2 (7 cm³) added to precipitate the required salt. The solid product was washed with back-condensed solvent and dried in vacuo. Yields, analyses and colours are given in Table 1.

IR: (X = CF₃), ν_{max} 1517m, 1432m, 1410m, 1320s (br), 1180s (br), 1120s (br), 1070s, 1020m, 985s, 965w, 915m, 890w, 880w, 850s, 835w, 830w, 800s, 770w, 695vs (br), 670m, 632m, 588m, 570w, 442m and 388vs; (X = Br), 1587s, 1418s, 1395m, 1312w, 1287w, 1212w, 1195vw, 1187m, 1180w, 1125w, 1075s, 1014m, 986s, 914m, 890w, 842s, 835s, 830m, 820m, 800s, 715s (br), 690vs (br), 670s, 628m, 590w, 580w, 490m, 440m and 398vs; (X = Cl), 1592s, 1420s, 1400s, 1315w (br), 1288m, 1212m, 1185m, 1127vw, 1110vw, 1095s, 1017m, 987s, 912m, 890m, 880w, 840s, 833w, 820m, 815w, 800s, 710s, 690vs (br), 672s, 629m, 620m, 593w, 580w, 500m, 492m, 443s and 400vs; (X = F), 1605s, 1600 (sh), 1518w(br), 1430s, 1410s, 1315m, 1305m, 1253s, 1215w, 1165 (sh), 1150s, 1110m, 988s, 980 (sh), 950w, 914m, 898m, 890w, 845s, 840w, 820m, 815w, 783s, 715s, 690s (br), 675s, 632m, 620m, 570m, 515m, 447m, 438m and 400s; (X = MeS), 1586m, 1579 (sh), 1420m, 1390s, 1198m, 1092s, 975m (br), 910w (br), 890w, 827m, 790m, 695vs (br), 625w, 548w (br), 494vw, 480vw, 440m and 397vs (br); (X = Me), 1605s, 1515w, 1400s, 1320w, 1212m,
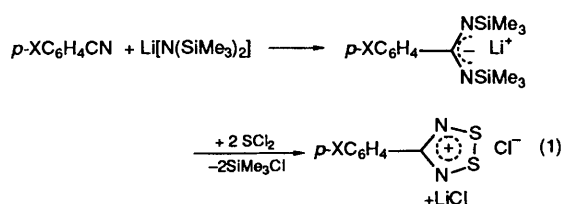
1185s, 995w, 980w, 915w, 890w, 835w, 810s, 800m, 780w, 690vs (br), 630m, 600w, 565w, 485w, 440m and 397s; (X = MeO), 1610m, 1435m, 1392s, 1335w, 1320m, 1310m, 1285m, 1270m, 1178s, 1125w, 1018w, 1005vw, 985m, 920w, 890w, 832s, 805m, 785m, 715s, 690s (br), 672m, 630w, 620w, 575w, 520vw, 440m and 397s cm⁻¹.

[Na(18-crown-6)][PhCNSSN]. A solution of (PhCNSSN)₂ (0.18 g, 0.5 mmol), 18-crown-6 (0.26 g, 1 mmol) and sodium amalgam (2.5% Na, 2 g, 2.2 mmol Na) in tetrahydrofuran (thf) (25 cm³) was stirred for 2 h at 21 °C. The resulting yellow-brown solution was filtered off and dried in vacuo to yield a yellow gum. Tetrahydrofuran was added and the solution cooled to −30 °C for 12 h to yield a yellow microcrystalline solid which was filtered off, washed with cold thf (2 × 2 cm³) and dried in vacuo. Yield 0.08 g, 17% (Found: C, 49.8; H, 6.0; N, 6.5; Na, 5.0; S, 14.7. Calc.: C, 48.7; H, 6.2; N, 6.0; Na, 4.9; S, 13.7%). IR: ν_{max} 3040 (sh), 1503s, 1482s, 1455s, 1414w, 1372m, 1349m, 1320w, 1301s, 1288s, 1247m, 1168w, 1110vs, 1067m, 1055m, 1021m, 961s, 937s, 914 (sh), 826m, 782w, 768s, 748w, 708s, 696m, 659w, 648w, 612s, 552m and 511m cm⁻¹.

Results and Discussion

Preparations.—The compounds [p-XC₆H₄CNSSN]Cl were synthesised in 55–77% isolated yield, using an amended[2d]

version of the literature route.[15] The parent nitrile was treated with Li[N(SiMe₃)₂] in Et₂O to form an N-lithio compound which was then treated with SCl₂ [equation (1)]. Separation of

$$p\text{-XC}_6\text{H}_4\text{CN} + \text{Li[N(SiMe}_3\text{)}_2] \longrightarrow p\text{-XC}_6\text{H}_4\!-\!\overset{\text{NSiMe}_3}{\underset{\text{NSiMe}_3}{\text{C}_{\phantom{\text{Li}^+}}}}\!\!\text{Li}^+$$

$$\xrightarrow[-2\text{SiMe}_3\text{Cl}]{+2\text{ SCl}_2} \; p\text{-XC}_6\text{H}_4\!-\!\overset{\text{N}-\text{S}}{\underset{\text{N}-\text{S}}{\text{C}\,\overset{\cdot}{\overset{}{\boxed{\cdot}}}}}\; \text{Cl}^- \quad (1)$$
$$+\text{LiCl}$$

the resultant $[p\text{-XC}_6\text{H}_4\overline{\text{CNSSN}}]\text{Cl}$ from LiCl was achieved by exhaustive SO₂ extraction. Metathesis of these salts with


(a)

(b)

(c)

E /V vs. SCE
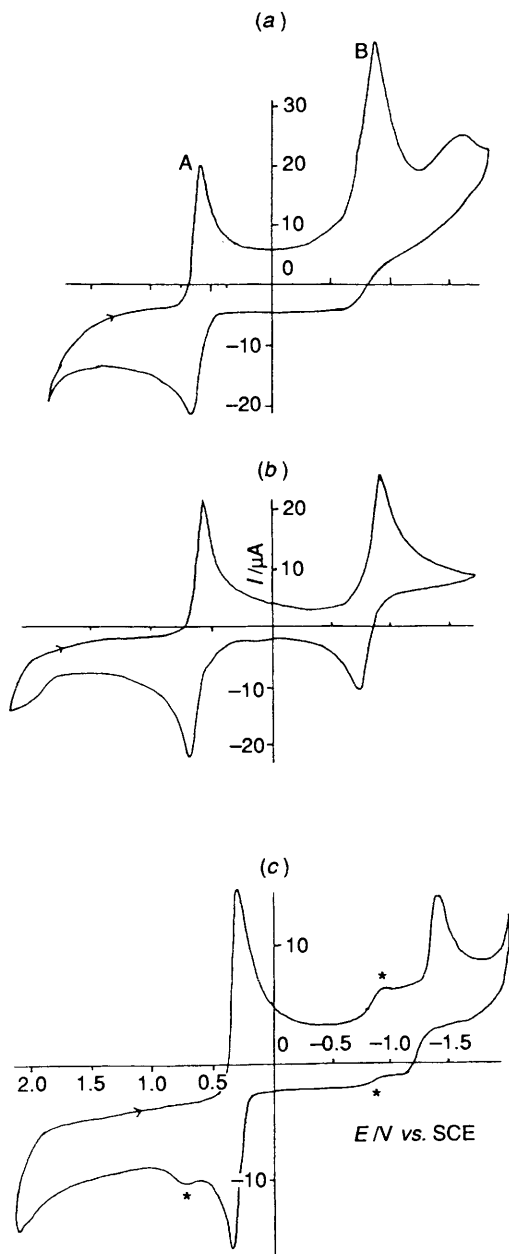
Fig. 2 Cyclic voltammograms recorded at −10 °C, using 0.1 mol dm⁻³ [NBu₄][BF₄] supporting electrolyte: (a) [PhCNSSN][AsF₆], (b) (PhCNSSN)₂ and (c) [PhCNSNS][AsF₆] (* indicates peaks attributable to the PhCNSSN ring system, formed by rearrangement of the [PhCNSNS]˙ radical in solution)

AgAsF₆ in liquid SO₂ provided the corresponding hexafluoroarsenate(v) salt in high yield, typically ca. 80%. The analogous 1,3,2,4-dithiadiazolylium salts were formed by the cycloaddition reaction of [SNS][AsF₆] with the parent nitrile in a similar manner to those previously reported.[2,3,13,14,17] The yield, analysis and colour for each of these compounds are shown in Table 1.

Cyclic Voltammetry (CV) of 1,2,3,5-Dithiadiazolylium Salts.— A typical cyclic voltammogram of a 1,2,3,5-dithiadiazolylium salt, [PhCNSSN][AsF₆], is shown in Fig. 2(a) and shows a reversible reduction process (A) at 0.62 ± 0.06 V (depending on the nature of the aryl substituent). This redox process can be attributed to the formation and reoxidation of the dithiadiazolyl radical, [RCNSSN]˙ (R = p-XC₆H₄) [equation (2)]. A second
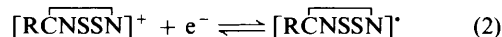
$$[\text{RCNSSN}]^+ + e^- \rightleftharpoons [\text{RCNSSN}]^{\boldsymbol{\cdot}} \quad (2)$$

irreversible process (B) is also observed and this can be attributed to the formation of the dithiadiazolide anion, [RCNSSN]⁻ [equation (3)]. The apparent irreversible nature

$$[\text{RCNSSN}]^{\boldsymbol{\cdot}} + e^- \rightleftharpoons [\text{RCNSSN}]^- \quad (3)$$
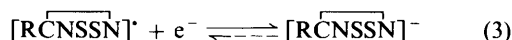
of this second process indicates further rapid reaction of the reduced species [RCNSSN]⁻ on the CV time-scale (seconds). One such possibility is a rapid quenching reaction of the reduced anionic species which may react with [RCNSSN]⁺ cations in the bulk solution [equation (4)]. The $E_{\frac{1}{2}}$(red)

$$[\text{RCNSSN}]^+ + [\text{RCNSSN}]^- \longrightarrow 2\,[\text{RCNSSN}]^{\boldsymbol{\cdot}} \quad (4)$$
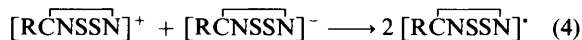
potentials for these salts are given in Table 2.

In comparison, CV studies of the neutral dithiadiazolyl radical (PhCNSSN)₂ [Fig. 2(b)] show that formation of both the dithiadiazolylium cation and dithiadiazolide anion are reversible processes. The unexpected change in stability of the dithiadiazolide anion can be attributed to the nature of the solution; [RCNSSN]⁻, formed during CV studies of the [RCNSSN]˙ radical, cannot be quenched by dithiadiazolylium cations since these are not present in the bulk solution.

A more detailed study of the redox properties of these dithiadiazolylium cations showed minor variations in the half-wave reduction potentials, $E_{\frac{1}{2}}$(red), with p-nitro, cyano and trifluoromethyl derivatives having slightly higher values than the corresponding methoxy and methyl derivatives ($\Delta E \leqslant 0.1$ V). Such variations in $E_{\frac{1}{2}}$(red) appear to be a function of the substituent and were independent of temperature [there was no significant variation in $E_{\frac{1}{2}}$(red) for any particular substituent group as a function of temperature, in the range −15 to +5 °C].

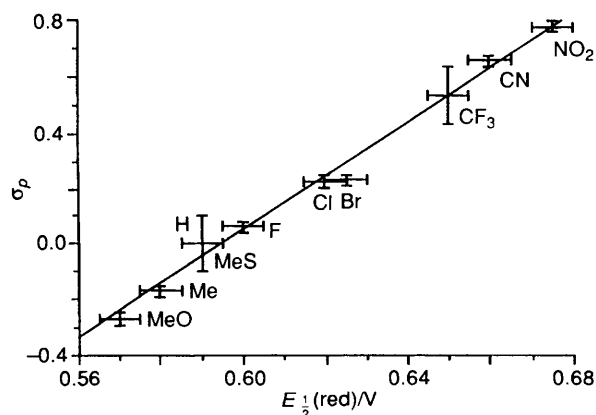Fig. 3 Plot of $E_{\frac{1}{2}}$(red) against σ_p for a series of aryl-1,2,3,5-dithiadiazolylium cations, as the hexafluoroarsenate(v) salts

Table 2 The $E_{\frac{1}{2}}$(red) values for some aryl-1,2,3,5- and 1,3,2,4-dithiadiazolylium cations, as the hexafluoroarsenate(v) salts

	$E_{\frac{1}{2}} \pm 0.005/V$		
X	[p-XC₆H₄C̄NSSN̄][AsF₆]	[p-XC₆H₄C̄NSNS̄][AsF₆]	$\sigma_p{}^a$
MeO	0.570	0.290	-0.268 ± 0.020
Me	0.580	0.300	-0.170 ± 0.020
MeS	0.590	0.310	0.000 ± 0.100
H	0.590	0.330	0.000
F	0.600	0.340	0.062 ± 0.020
Cl	0.620	0.350	0.227 ± 0.020
Br	0.625	0.350	0.232 ± 0.020
C̄NSSN̄⁺	0.650		0.537 ± 0.005^b
CF₃	0.650	0.380	0.540 ± 0.100
C̄NSNS̄⁺		0.385	0.57 ± 0.02^b
CN	0.660		0.660 ± 0.020
NO₂	0.675	0.400	0.778 ± 0.020

a Taken from ref. 18 except where indicated. *b* This work.

The strong correlation between $E_{\frac{1}{2}}$(red) and the Hammett values [18] σ_p (Fig. 3) for the p-substituent indicates a linear free-energy relationship between the redox potential and the functional group. Such a correlation is hardly unexpected since the free energy of the system, ΔG, is related to the electrode potential via the relationship $\Delta G^{\ominus} = -nE^{\ominus}F$. However, the correlation is indicative of a similar reaction mechanism occurring throughout this reaction series, viz a study of the electroactive CN_2S_2 functionality.

Cyclic Voltammetry of 1,3,2,4-Dithiadiazolylium Salts.—Cyclic voltammetry studies of these salts showed similar electrochemical behaviour to their 1,2,3,5-dithiadiazolylium isomers, within the half-wave reduction potential region +0.29 to +0.43 V. The $E_{\frac{1}{2}}$(red) potentials for these salts are given in Table 2. Although the deviations from linearity are more noticeable (correlation factor, |r|, for the 1,2,3,5-dithiadiazol-yl/-ylium ring system is 0.995 whilst that for the 1,3,2,4-dithiadiazol-yl/-ylium ring system is 0.980) there is still a strong correlation between $E_{\frac{1}{2}}$(red) and σ_p values (Fig. 4).

In the case of the 1,3,2,4-dithiadiazol-yl/-ylium heterocycle the functional group has a more marked effect on the $E_{\frac{1}{2}}$(red) potentials with an 8% larger ρ value* than the corresponding 1,2,3,5-dithiadiazol-yl/-ylium system (ρ = 0.111 and 0.103 respectively). Such a difference can perhaps be attributed to the nature of the reduction process, i.e. partial filling of the dithiadiazolylium lowest unoccupied molecular orbital (LUMO). Molecular orbital calculations on [PhC̄NSSN̄]⁺ [5a] show that the 1,2,3,5-dithiadiazolylium cations possess a LUMO with a nodal plane through the heterocyclic ring carbon atom, whereas 1,3,2,4-dithiadiazolyl radicals, formed by partial occupation of the C̄NSNS̄⁺ LUMO, show some unpaired spin density on the heterocyclic carbon (see Fig. 5). Such a nodal plane on the [RC̄NSSN̄]⁺ singly occupied molecular orbital (SOMO) prohibits[4a,20] (at least to a first-order approximation) through-bond interactions between the heterocyclic ring and the aryl substituent. This is not the case for the 1,3,2,4-dithiadiazolylium ring system, and partial occupancy of the [RC̄NSNS̄]⁺ LUMO leads to some spin density at the heterocyclic carbon centre and thus a larger value for ρ.
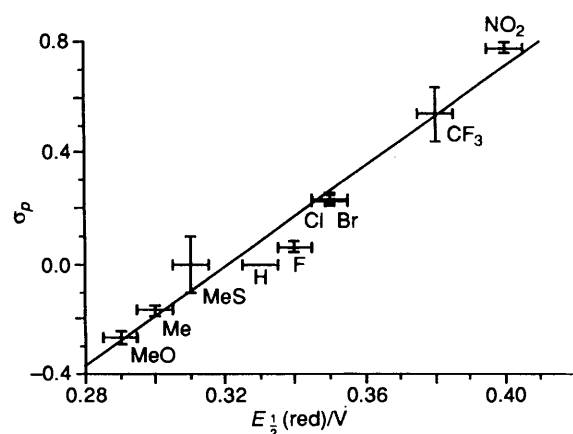
Using this correlation (Figs. 3 and 4) and cyclic volt-

Fig. 4 Plot of $E_{\frac{1}{2}}$(red) against σ_p for a series of aryl-1,3,2,4-dithiadiazolylium cations, as the hexafluoroarsenate(v) salts
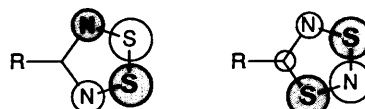
Fig. 5 The LUMOs of the [RC̄NSSN̄]⁺ and [RC̄NSNS̄]⁺ cations (R = p-XC₆H₄) respectively

ammograms of p-[S̄NSNCC₆H₄C̄NSNS̄][AsF₆]₂ and p-[N̄SSNCC₆H₄C̄NSSN̄][AsF₆]₂, the σ_p values for C̄NSSN̄⁺ and C̄NSNS̄⁺ rings can be calculated as +0.537 ± 0.005 and +0.57 ± 0.02 respectively.

Preparation of [Na(18-crown-6)][PhC̄NSSN̄].—Since cyclic voltammetry studies on (PhC̄NSSN̄)₂ indicated the presence of a stable dithiadiazolide anion a preparative-scale reaction was attempted. Reduction of (PhC̄NSSN̄)₂ in thf with sodium amalgam in the presence of 18-crown-6 at room temperature yielded a yellow-brown solution which afforded a viscous yellow oil on drying *in vacuo*. A small quantity of yellow microcrystalline solid was obtainable from this oil by cooling a concentrated thf solution to −30 °C. This material analysed as [Na(18-crown-6)][PhC̄NSSN̄] and showed IR bands attributable to co-ordinated 18-crown-6, consistent with the formation of a dithiadiazolide anion. Although stable in the solid state, this material was found to decompose in solution at room temperature and attempts to grow single crystals have so far been unsuccessful. However it is to be anticipated that the S–S

* The Hammett equation[19] may be written: $\log(k/k_0) = \sigma\rho$ where $\log(k/k_0)$ represents the free-energy term, σ is the substituent constant and ρ is a reaction constant reflecting the susceptibility of the electroactive species to electronic effects.

distance in this compound will be larger than d_{SS} in both [PhCNSSN][AsF$_6$][20] (*ca.* 2.017 Å) and (PhCNSSN)$_2$[6] (*ca.* 2.09Å) since the highest occupied molecular orbital (HOMO) of this anion (the same as the LUMO of the dithiadiazolylium cation) is antibonding with respect to S–S.

Conclusion

Novel aryl-1,2,3,5- and -1,3,2,4-dithiadiazolylium salts have been prepared and products of both isomeric types exhibit a linear free-energy relationship between the half-wave reduction potential and the Hammett value, σ_p, for the *para*-substituent. Such a relationship should prove useful in the design and synthesis of charge-transfer salts, where slight modifications of the structure may enhance the observed properties. Cyclic voltammetry studies of the phenyl-1,2,3,5-dithiadiazolyl radical indicated that the dithiadiazolide anion is a stable entity and this anion was subsequently isolated in low yields. Our present work involves the synthesis and characterisation of the analogous substituted dithiadiazolyl radicals and dithiadiazolide anions in the solid state.

Acknowledgements

References

1 (a) A. J. Banister and J. M. Rawson, *Chem. Br.*, 1992, 148; (b) A. J. Banister and J. M. Rawson, in *The Chemistry of Inorganic Ring Systems*, ed. R. Steudel, Elsevier, Amsterdam, 1992, p. 323; (c) A. W. Cordes, R. C. Haddon and R. T. Oakley, in *The Chemistry of Inorganic Ring Systems*, ed. R. Steudel, Elsevier, Amsterdam, 1992, p. 295.

2 (a) A. J. Banister, J. M. Rawson, W. Clegg and S. L. Birkby, *J. Chem. Soc., Dalton Trans.*, 1991, 1099; (b) A. J. Banister, I. Lavender, J. M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1992, 859; (c) C. M. Aherne, A. J. Banister, A. W. Luke, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1277; (d) A. J. Banister, I. Lavender, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1449.

3 S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1991, 369.

4 (a) A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, 113, 582; (b) M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. Tycko, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, 113, 3559; (c) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc.*, 1992, 114, 5000.

5 (a) A. J. Banister, M. I. Hansford, Z. V. Hauptman, A. W. Luke, S. T. Wait, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1990, 2793; (b) W. Clegg, S. L. Birkby, A. J. Banister, J. M. Rawson, S. T. Wait, P. Rizkallah, M. M. Harding and A. J. Blake, *Acta Crystallogr., Sect. C*, submitted for publication.

6 A. Vegas, A. Pérez-Salazar, A. J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.

7 A. J. Banister, M. I. Hansford, Z. V. Hauptman, S. T. Wait and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1989, 1705.

8 A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, 31, 1802.

9 M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1675.

10 A. J. Banister, Z. V. Hauptman, A. G. Kendrick and R. W. H. Small, *J. Chem. Soc., Dalton Trans.*, 1987, 915.

11 A. J. Banister, R. G. Hey, G. K. MacLean and J. Passmore, *Inorg. Chem.*, 1982, 21, 1679.

12 A. J. Banister, N. R. M. Smith and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1983, 1181.

13 B. Ayres, A. J. Banister, P. D. Coates, M. I. Hansford, J. M. Rawson, C. E. F. Rickard, M. B. Hursthouse, K. M. A. Malik and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1992, 3097.

14 S. Parsons, J. Passmore, M. J. Schriver and X. Sun, *Inorg. Chem.*, 1991, 30, 3342.

15 P. D. B. Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, 111, 9276.

16 R. W. H. Small, A. J. Banister and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.

17 G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405; W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69; N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.

18 C. G. Swain and E. C. Lupton, jun., *J. Am. Chem. Soc.*, 1968, 90, 4328.

19 *The Penguin Dictionary of Chemistry*, ed. D. W. A. Sharp, Penguin Books Ltd., London, 1983.

20 K. Bestari, G. Ferguson, J. F. Gallagher and R. T. Oakley, *Inorg. Chem.*, 1992, 31, 442.