Dalton Communications

Convenient Preparations of the Mixed 1,3,2,4-/1,2,3,5-Dithiadiazolylium Salt $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}][AsF_6]_2$ and the First Mixed Free Radical, *p*-$[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]^{2\cdot}$

Arthur J. Banister,*[a] Ian Lavender,[a] Jeremy M. Rawson[a] and Roger J. Whitehead[b]
[a] *Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK*
[b] *Department of Physics, Durham University, South Road, Durham DH1 3LE, UK*

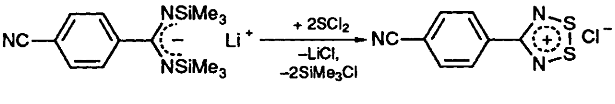
The salt [*p*-$NCC_6H_4-\overline{CNSSN}$]Cl {prepared by reaction of Li[*p*-$NCC_6H_4C(NSiMe_3)_2$] with SCl_2} was converted into [*p*-$NCC_6H_4-\overline{CNSSN}$]$AsF_6$ (with $AgAsF_6$) and then reacted with [SNS]AsF_6 to provide $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}][AsF_6]_2$ in 92% recovered yield. Complete reduction of this material produced the first mixed 1,3,2,4-/1,2,3,5-dithiadiazole diradical, $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]^{2\cdot}$.

Recent developments in the chemistry of CN_2S_2 heterocycles have led to the synthesis of a variety of both multi(1,2,3,5- and multi(1,3,2,4-dithiadiazolylium) cations.[1–6] Reduction of these materials leads to the formation of the corresponding multi-(dithiadiazoles)[1,5,6] some of which form polymeric arrays in the solid state. Such arrays are an important feature in the design of organic metals[7] and recently the selenium analogue of $C_6H_4(\overline{CNSSN})_2$ has been shown to be a room-temperature semiconductor.[5]

The formation of mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium salts was therefore of particular interest since this will facilitate the preparation of not only mixed dithiadiazole multiradicals, but it also offers the possibility of forming the intermediate radical cations because the reduction potentials for aromatic substituted 1,2,3,5- and 1,3,2,4-dithiadiazolylium cations are typically separated by *ca.* 0.35 V.[8] In contrast both phenylenebis(1,3,2,4- and -bis(1,2,3,5-dithiadiazolylium) dications show a single two-electron reduction process to the corresponding bis-(dithiadiazoles).

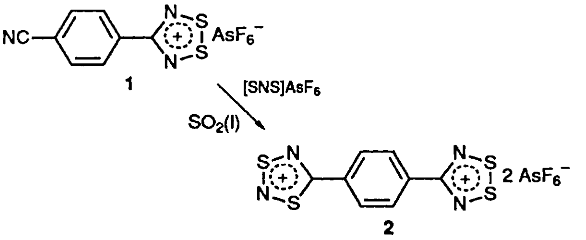
Passmore and co-workers[4] have previously prepared the radical cation $[\overline{SNSNC}-\overline{CNSSN}]^{\cdot+}$ and the dication $[\overline{SNSNC}-\overline{CNSSN}]^{2+}$. However their route (with overall yield of 39%) is somewhat circuitous since it involves partial reduction, subsequent rearrangement and then reoxidation of $[\overline{SNSNC}-\overline{CNSNS}]^{2+}$. We therefore sought a general convenient synthesis of mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium salts and their reduced species. We now describe a convenient synthesis of [*p*-$NCC_6H_4-\overline{CNSSN}$]$AsF_6$ **1** and its subsequent reaction with [SNS]AsF_6 to provide $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]$-$[AsF_6]_2$ **2** in high yield. The reduction chemistry of **2** is discussed in the light of cyclic voltammetry (CV) and ESR data.

Oakley and co-workers[9] have previously shown that reaction of persilylated amidines, $RC(=NSiMe_3)N(SiMe_3)_2$ with SCl_2 provides a convenient high-yield route to dithiadiazolylium salts, [R$\overline{CNSSN}$]Cl. In some cases (R = *p*-$O_2NC_6H_4$ or *p*-NCC_6H_4) isolation of this amidine is not possible.[10] However we found that reaction of the intermediate, Li[$RC(NSiMe_3)_2$], with a slight excess of SCl_2 also provided the corresponding dithiadiazolylium chloride in high yield [equation (1)].



(1)

Conversion into the corresponding AsF_6^- salt **1** was readily achieved by simple metathesis with $AgAsF_6$ in MeCN. Salt **1** reacts with [SNS]AsF_6 in liquid SO_2 over a period of 12 h and precipitates the mixed 1,3,2,4-/1,2,3,5-dithiadiazolylium dication as the pale yellow AsF_6^- salt **2**† [equation (2)]. Cyclic voltammetry of **2** shows two different reversible processes (Fig. 1) with E_1 and E_2 being associated with the 1,2,3,5-dithiadiazole/-olylium and 1,3,2,4-dithiadiaz-ole/-olylium redox processes respectively.



1

2

(2)

Metathesis of salt **2** with NBu_4Cl in CH_2Cl_2 provided

---

† *Preparation of* $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}][AsF_6]_2$.—The salts [SNS]$AsF_6$ (0.554 g, 2 mmol) and [*p*-$NCC_6H_4-\overline{CNSSN}$]$AsF_6$ (0.790 g, 2 mmol) were placed in one limb of a two-limbed reaction vessel and liquid SO_2 condensed on. The reagents were stirred at room temperature for 18 h during which time a pale yellow precipitate formed under a red solution. The SO_2 was removed by vacuum transfer and the residual solid was then washed with CH_2Cl_2 (3 × 5 cm^3, by back condensation) leaving a yellow powder. Yield 1.220 g, 92%. IR ν_{max} at 1518m, 1400s, 1302w, 1205w, 1162m, 1020w, 990s, 922s, 888w, 852s, 845m, 832w, 800s, 749m, 700vs, 670s, 630w, 590w, 560w, 440w and 400s cm^{-1} {Found: C, 14.55; N, 8.50; H, 0.65. Calc. for $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}][AsF_6]_2$: C, 14.50; N, 8.45; H, 0.65%}.

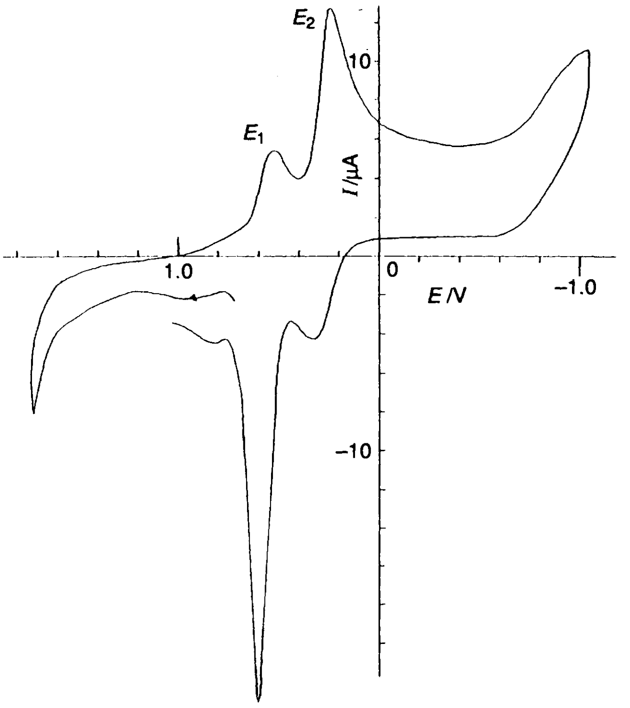
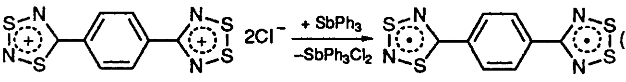


Fig. 1 Cyclic voltammogram of $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}][AsF_6]_2$ in MeCN at −10 °C using $[NBu_4]BF_4$ as electrolyte; half-wave potentials E_1(red) = 0.595 V, E_2(red) = 0.303 V *vs.* a saturated calomel electrode

$[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]Cl_2$ in high yield, and this salt was reduced with $SbPh_3$ to provide the mixed diradical $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]^{2\bullet}$ as an insoluble black powder [equation (3)]. The ESR spectrum of this material showed two signals of approximately 1:1 intensity: a five-line 1:2:3:2:1 pentet overlapping with a 1:1:1 triplet (Fig. 2). On standing the intensity of the triplet diminished to leave the simple five-line pattern, indicative of rearrangement[11] from the less-stable 1,3,2,4 isomer to the 1,2,3,5-dithiadiazole ring system, the ESR spectrum of the rearrangement product being consistent with literature data[5] (a_N = 0.51 mT, g = 2.011).



(3)

3

Further studies into the nature of *ortho*, *meta* and *para* derivatives of mixed 1,3,2,4-/1,2,3,5-dithiadiazole and the preparation of the radical cations $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]^{\bullet +}$ are underway.

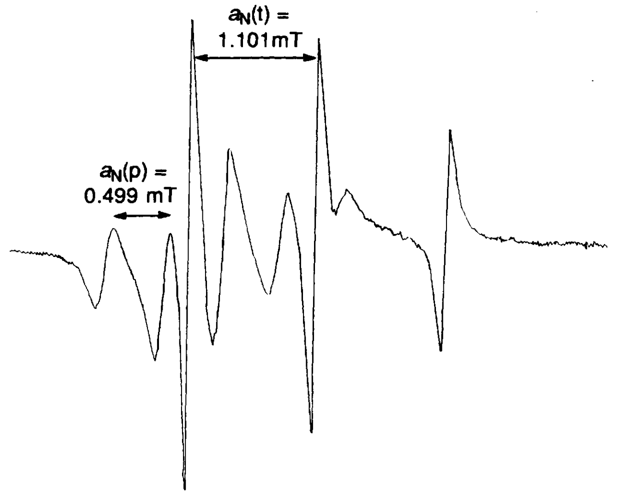


Fig. 2 The ESR spectrum of $[\overline{SNSNC}-C_6H_4-\overline{CNSSN}]$ in toluene

Acknowledgements

We thank the SERC for funding and Professor R. T. Oakley for his comments and interest in this work.

References

1 A. J. Banister, J. M. Rawson, W. Clegg and S. L. Birkby, *J. Chem. Soc., Dalton Trans.*, 1991, 1099.
2 A. J. Banister, I. Lavender, J. M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1992, 859.
3 C. Aherne, A. J. Banister, A. W. Luke, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1277.
4 S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1991, 369.
5 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.
6 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.
7 R. C. Haddon, *Nature (London)*, 1975, **256**, 394.
8 A. J. Banister and J. M. Rawson, *Chem. Br.*, 1992, 148.
9 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.
10 R. T. Boeré, R. T. Oakley and R. W. Reed, *J. Organomet. Chem.*, 1987, **331**, 161.
11 W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69.

Received 16*th January* 1992; *Communication* 2/00254J