Electron Spin Resonance Spectroscopy of CF₃CNSSN' and C₆F₅CNSSN' Free Radicals

Shirley A. Fairhurst and Leslie H. Sutcliffe*

Chemistry Department, University of Surrey, Guildford, Surrey GU2 5XH, UK

Keith F. Preston

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, K1A 0R6, Canada

Arthur J. Banister, Andrew S. Partington and Jeremy M. Rawson Chemistry Department, University of Durham, Durham DH1 3LE, UK

Jack Passmore and Melbourne J. Schriver

Chemistry Department, University of New Brunswick, Fredericton, New Brunswick, E38 6E2, Canada

Solution and powder ESR spectra of the 4-trifluoromethyl-1,2,3,5-dithiadiazolyl and 4-pentafluorophenyl-1,2,3,5dithiadiazolyl free radicals were analysed. Comparison of the ESR parameters with those obtained for the protonated equivalents shows that fluorination produces a drift of unpaired electron spin density away from the nitrogen $2p_x$ orbitals towards sulphur $3p_x$ orbitals (x is the direction perpendicular to the heterocyclic ring), consistent with an increase in electronegativity of the substituent. The fluorinated radicals dimerize more readily than their protonated counterparts.

KEY WORDS ESR Isotropic spectra Powder spectra Dithiadiazolyl radicals Dimerization

INTRODUCTION

Sulphur-nitrogen chemistry is a very active field of research with regard to both closed-shell compounds¹ and free radicals.² The largest groups of the latter are the 1,3,2-dithiazolodin-2-yl, 1,3,2-dithiazol-2-yl, 1,3,2,4-dithiadiazolyl and 1,2,3,5-dithiadiazolyl radicals.² In this paper we report detailed ESR spectroscopic results for two of the latter type of radicals having fully-fluorinated substituents at the 4-position, namely 4-trifluoromethyl-1,2,3,5-dithiadiazolyl (1) and 4-pentafluorophenyl-1,2,3,5-dithiadiazolyl (2). The results obtained are compared with those we found earlier³ for the 4-substituted radicals 4-methyl- (3) and 4-phenyl-1,2,3,5-dithiadiazolyl (4).



EXPERIMENTAL

Materials

Preparation of CF₃CNSSN[•] (1). CF₃CSNSN · AsF₆ (0.72 g, 2.0 mol), prepared as described previously,⁴ was added to Na₂S₂O₄ (1.0 g, 5.8 mol) in liquid SO₂ (3.2 g),

giving a clear, colourless solution that turned opaque red-black in 2 h. The red-black CF_3CNSSN^* (0.25 g, 1.5 mol, 73% yield) was recovered by fractional distillation, leaving an insoluble white solid (0.91 g), which was found to be a mixture of $Na_2S_2O_4$ and $NaAsF_6$ (IR). The red-black solid (m.p. 37 °C) was identified by elemental analysis and by a comparison of its mass spectrum with previously obtained results.⁵

Preliminary ESR measurements⁶ showed that the enthalpy of dimerization is similar to that of $C_6H_5CNSSN^2$; dissociation of dimers in solution is complete above about 270 K.

Preparation of C_6F_5CNSSN' (2). $(C_6F_5CNSSN)Cl$ was prepared from C_6F_5CN (Aldrich), $Li[N(SiMe_3)_2]$ (Aldrich) and SCl₂ (BDH) in a similar manner to other aryl-substituted-1,2,3,5-dithiadiazolylium salts. Reduction of this salt with a Zn-Cu couple (Alfa Inorganics) in liquid SO₂ produced a deep purple solution over a period of 24 h. After filtering, the solution was evaporated to dryness in vacuo. The solid was sublimed under a static vacuum (0.1 Torr 80°C) to yield (52%) large, red, well formed, diamond-shaped crystals of $(C_6F_5CNSSN)_2$. All solvents were dried and degassed before use. Single crystals of the dimer do not give an ESR signal but the solid dissociates reversibly in solution to give high concentrations of the free radical. This solution property is similar to that of the related radical 4, where it was found³ the dissociation of dimers is virtually complete in solution above about 250 K.

EPR spectroscopy

Isotropic spectra were obtained from solutions of the radicals in either perdeuteriotoluene (Aldrich) or CFCl₃

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^{*} Author to whom correspondence should be addressed.

Parameter	CF ₃ CNSSN [.] (1)	CH₃CNSSN [™] (3)	C ₆ F ₅ CNSSN [•] (2)	C ₆ H ₆ CNSSN ^{. ь} (4)
Temperature (K)	193	203	219	205
$\boldsymbol{g}_{\mathrm{iso}}$	2.01060	2.0104	2.01012	2.01019
a(N)	0.490	0.538	0.505	0.517
a(F)	0.162	_	0.161	_
a(H)		0.205		\sim 0.02
<i>a</i> (S)	0.679	0.645	0.678	0.617
^a Hyperfine interact ^b Taken from Ref. 3	ions are in mT.			

 Table 1. Isotropic ESR spectral parameters^a of some 4-substituted 1,2,3,5dithiadiazolyl radicals in perdeuteriotoluene

(Aldrich) which had been degassed on a vacuum system with a minimum of five freeze-pump-thaw cycles.

X-band spectra were recorded with (i) a Jeol RE1X ESR spectrometer equipped with a Jeol ES-FC5 NMR gaussmeter and a Jeol DVT-2 temperature controller or (ii) a Varian E-4 spectrometer fitted with a Bruker ER 035M-1000 NMR gaussmeter and Varian V-4540 temperature controller.

RESULTS

$CF_3CNSSN^{\circ}(1)$

In order to obtain a well resolved isotropic spectrum, it was necessary to cool the sample (as was also found necessary for 3^3) to about -50 °C. At this temperature, optimum conditions are realized for minimum line width: the decrease in line width from electron exchange with decreases of temperature is balanced by the increase in line width from modulation of the hyperfine coupling. As can be seen from Fig. 1, the isotropic spectrum comprises a 1:2:3:2:1 quintet of 1:3:3:1 quartets and is similar to that observed for CH₃CNSSN':³ in Fig. 1 the spectrum is distorted at the



Figure 1. First-derivative X-band ESR spectrum of CF_3CNSSN' in CFCl₃ at 153 K. The low-field part of the spectrum (run at higher gain) shows some of the sulphur-33 satellite lines.

high fields owing to the onset of asymmetric line broadening. The spectral parameters derived from the spectrum are listed in Table 1. The spectrum from a frozen perdeuteriotoluene solution is well resolved, showing hyperfine interactions from the perfluoromethyl group, as can be seen from Fig. 2, where it is shown along with a computer-simulated spectrum based on the parameters given in Table 2.

$C_6F_5CN\overline{SSN}$ (2)

Again, low temperatures are necessary to obtain a well resolved solution spectrum (illustrated in Fig. 3), which shows that it comprises a 1:2:3:2:1 quintet of 1:2:1 triplets, the latter arising from two equivalent



Figure 2. First-derivative X-band ESR powder spectrum of CF_3CNSSN' in perdeuteriotoluene at 123 K: (a) experimental; (b) computer simulation.

Parameter	CF ₃ CNSSN	CH ₃ CNSSN [·] ^b	C ₆ F ₅ CNSSN	C ₆ H ₅ CNSSN [·] ^b
raianietei	(1)	(3)	(2)	()
Temperature (K)	123	112	123	109
g_{xx}	2.0022	2.0026	2.0025	2.0021
$g_{\gamma\gamma}$	2.0080	2.0090	2.0085	2.0078
g ₂₂	2.0216	2.0215	2.0220	2.0218
$\langle g \rangle$	2.0106	2.0110	2.0110	2.0106
$a(N) + A_{xx}(N)$	1.350	1.43	1.384	1.400
$a(N) + A_{yy}(N)$	0.004	0.08	0.100	0.107
$a(N) + A_{zz}(N)$	0.036	0.11	0.031	0.035
$\langle a(N) \rangle$	0.463	0.541	0.505	0.514
$a(F) + A_{xx}(F)$	0.139		0.157	
$a(F) + A_{yy}(F)$	0.139		0.093	—
$a(F) + A_{zz}(F)$	0.203	—	0.232	
$\langle a(F) \rangle$	0.160		0.161	
$a(H) + A_{xx}(H)$	_	0.242		~ 0
$a(H) + A_{yy}(H)$		0.242		\sim 0
$a(H) + A_{12}(H)$	_	0.242		~ 0
⟨a(H)⟩		0.242		~ 0
^a Hyperfine interacti ^b Taken from Ref. 3.	ons in mT.			

 Table 2. Anisotropic ESR spectral parameters^a from some 4-substituted

 1,2,3,5-dithiadiazolyl radicals in a perdeuteriotoluene matrix

ortho-fluorine nuclei. The powder spectrum (see Fig. 4) has far more splittings than were observed for radical 4^3 owing to significant p spin density being located on the fluorine nuclei.

DISCUSSION

g-Factors

From Tables 1 and 2, it can be seen that the isotropic g-factors and the principal values of the **g**-matrix are virtually identical for radicals 1–4. In all four radicals, the major shifts in g from the free-spin value are along the y and z axes. This observation has been explained^{8,9} in terms of spin-orbit interactions between the ${}^{2}A_{2}$



Figure 3. Second-derivative X-band ESR spectrum of $C_6F_5CNSSN^*$ in perdeuteriotoluene at 219 K.

ground state and excited states corresponding to filled orbitals (b₂ along y, a₁ along z). Sulphur makes the dominant contribution towards the g-shifts because of its large spin-orbital coupling constant. Since the SOMO of these radicals is *antibonding* between constituent atoms of the ring, increasing the electronegativity



Figure 4. First-derivative X-band ESR powder spectrum of C_6F_5CNSSN' in perdeuteriotoluene at 123 K: (a) experimental; (b) computer simulation.

of a substituent at the 4-position will result in a drift of unpaired electron spin away from the substituent towards the more electropositive atoms of the ring (i.e. sulphur). The hyperfine coupling constants (discussed below) clearly reflect this trend. The reverse trend will occur, of course, for the bonding orbitals. Shifts in qfrom the free spin value are, to first order, proportional to the energy gap between the states. Thus, unless the energy gap is modified drastically, changes in the 4substituent will have little influence on the g-matrix components because of opposing effects on sulphur 3p spin densities in the half-filled and the filled orbitals. This clearly is the case for radicals 1-4. It is unfortunate that, even at the *ab initio* level, spin density calculations are not trustworthy. Essentially, this is because the basis wave functions are inadequate close to the nucleus. Chipman¹⁰ has outlined the difficulties in predicting sorbital spin densities.

Nitrogen hyperfine interactions

There is considerable variation among the radicals 1-4 for the nitrogen isotropic interactions, the largest value being for the methyl-substituted radical and the smallest for the trifluoromethyl derivative. Earlier work³ showed that these interactions increase with increase in temperature: the hyperfine temperature coefficient is such that this conclusion would be the same even if the temperature variations listed in Table 1 were compensated for. The anisotropic hyperfine interactions for the xdirection, that is, at right-angles to the plane of the heterocyclic ring, follow at similar pattern. It should be noted that in the crystal of $(C_6H_5CNSSN)_2^{11}$ the phenyl and heterocyclic rings are approximately coplanar; the twist angle is 38.2° between the aryl and heterocyclic rings in $(C_6F_5\overline{CNSSN})_2$.¹² The more extensive π -electron system of radicals 2 and 4 does not appear to influence the spectra.

Sulphur hyperfine interactions

The isotropic sulphur coupling constants are greatest for the fluorinated radicals; hence it appears that fluorination draws s spin density away from nitrogen and increases it on sulphur. The low natural abundance of sulphur-33 made observation of anisotropic couplings impossible. However, if it is assumed that these couplings follow a pattern similar to that of the isotropic couplings, then stronger dimerization of the fluorinated radicals would be expected. The crystal structures^{11,12} of radicals 2 and 4 confirm this conclusion: the lengths of the long sulphur-sulphur bonds in 2 are 306.7 pm whereas in 4 they are 340.2 pm.

Fluorine hyperfine interactions

From Tables 1 and 2, it can be seen that both the isotropic and anisotropic interactions for this nucleus are surprisingly similar for radicals 1 and 2. In Fig. 2 the trifluoromethyl radical powder spectrum can be seen to have a 1:3:3:1 pattern for the fluorine splittings in the x direction, which shows that the trifluoromethyl group is freely rotating at 123 K. The powder spectrum of C₆F₅CNSSN' (see Fig. 4) can give no information on the presence of internal rotation of the aromatic ring or on the magnitude of the twist angle in the absence of internal rotation. The reason for this is that the two ortho-fluorine nuclei remain equivalent whatever the orientation or the rate of interconversion.

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REFERENCES

- 1. R. T. Oakley, Prog. Inorg. Chem. 36, 299 (1988).
- K. F. Preston and L. H. Sutcliffe, Magn. Reson. Chem. 28, 189 (1990).
- S. A. Fairhurst, K. M. Johnson, L. H. Sutcliffe, K. F. Preston, A. J. Banister, Z. V. Hauptman and J. Passmore, *J. Chem. Soc.*, *Dalton Trans.* 1465 (1986).
- S. Parsons, J. Passmore, M. J. Schriver and X. Sun, *Inorg. Chem.* 30, 3342 (1991).
- H. U. Hofs, J. W. Bats, R. Gleiter, G. Hartmann, R. Mews, N. Ecker-Maksic, H. Oberhammer and G. M. Sheldrick, *Chem. Ber.* 118, 3781 (1983).
- W. V. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, J. Chem. Soc., Chem. Commun. 69 (1987).
- C. M. Aherne, A. J. Banister, I. B. Gorrell, M. I. Hansford, Z. V. Hauptman, A. W. Luke and J. M. Rawson, *J. Chem. Soc.*, *Dalton Trans.* 967 (1993).
- F. L. Lee, K. F. Preston, A. J. Williams, L. H. Sutcliffe, A. J. Banister and S. T. Wait, *Magn. Reson. Chem.* 27, 1161 (1989).
- 9. K. F. Preston, J-P. Charland and L. H. Sutcliffe, *Can. J. Chem.* 66, 1299 (1988).
- 10. D. M. Chipman, J. Phys. Chem. 96, 3294 (1992).
- 11. A. Vegas, A. Pérez-Salazar, A. J. Banister and R. G. Hey, J. Chem. Soc., Dalton Trans. 1465 (1984).
- J. K. Howard, A. S. Batsanov, A. J. Holland, A. S. Partington, A. J. Banister and J. M. Rawson, to be published.