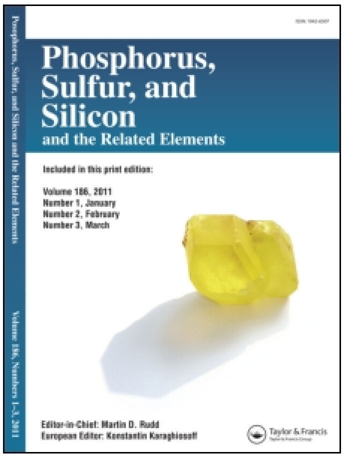

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Probing the Electronic Structure of the 1,3,5-Trithia-2,4,6-Triazapentalenyl Radical

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The electronic structure of the 1,3,5-trithia-2,4,6-triazapentalenyl radical **1** was probed by means of EPR spectroscopy and DFT calculations. The unpaired spin density is delocalised asymmetrically over the entire molecule with 84% based on the SNS fragment and 22% on the NSN fragment.

Keywords: EPR; DFT; dithiazolyl radical

INTRODUCTION

As a continuation of our work on thiazyl radicals as potential molecular magnetic materials[1,2] we have investigated the 1,3,5-trithia-2,4,6-triazapentalenyl radical **1** first reported by Wolmerhäuser[3]. Here we probe its detailed electronic structure through solution EPR experiments, supported by DFT calculations.

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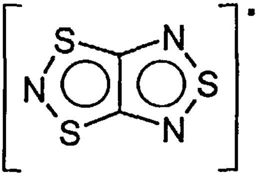

1

Figure 1: The 1,3,5-trithia-2,4,6-triazapentalenyl radical.

ELECTRONIC STRUCTURE OF 1

EPR studies

Solution EPR studies on 1 were performed on a CH_2Cl_2/toluene mixture. At room temperature, 1 exhibited a well-defined 1:1:1 triplet spectrum ($g_{iso} = 2.0053$, $a_{iso}^{N(1)} = 11.2$ G) consistent with coupling to the unique ^{14}N atom, N(1). No resolution of hyperfine coupling to the two N(2) atoms was observed and there was no improvement in resolution in the temperature range 300-240 K.

Frozen solutions at *ca.* 100 K exhibited rhombic EPR spectra ($g_1 = 2.0015$; $g_2 = 2.0046$; $g_3 = 2.0105$). Only the smallest g-value (g_1) exhibited an observable hyperfine coupling pattern: a triplet to the unique N(1) ($a_1^{N(1)} = 28.4$ G), further split into 1:2:3:2:1 pentets by a smaller coupling to the two equivalent N(2) nuclei of the thiadiazole ring ($a_1^{N(2)} = 2.5$ G). The N(2) hyperfine structure on g_1 is resolved clearly in the second derivative X-band spectrum (Figure 2). Hyperfine coupling to N(1) or N(2) is not observed on g_2 or g_3 implying much smaller coupling constants than those observed on g_1. The absence of hyperfine structure is entirely consistent with the unpaired electron residing in a π-type orbital with g_1 coparallel to the direction perpendicular to the plane of the molecule. This is in agreement with other studies on dithiazolyl radicals[2]. An analysis of the hyperfine coupling parameters from isotropic and anisotropic solution spectra was used to map the spin density distributions on N in 1.

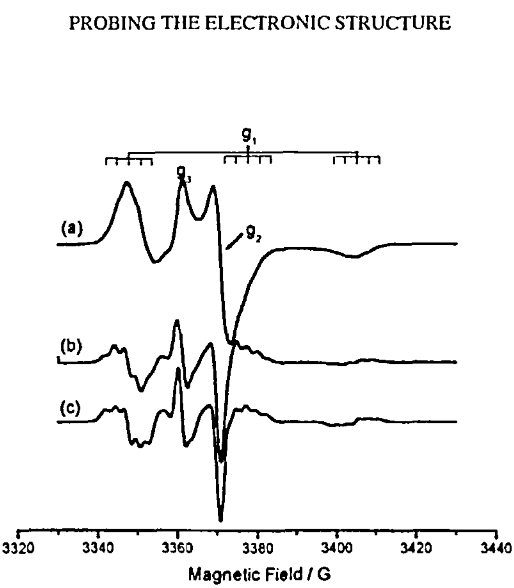

Figure 2: Frozen solution X-band EPR spectrum of **1** in CH$_2$Cl$_2$/toluene at 103 K; a) 1st derivative spectrum; b) 2nd derivative spectrum; c) 2nd derivative simulation.

DFT calculations

DFT calculations were carried out on **1** using the molecular geometry determined from the single crystal studies reported by Wolmershäuser[13]. These calculations indicate that the unpaired electron resides in a π^* orbital which is delocalised over the entire molecule (Fig. 2), with 84% based on the SNS fragment and just 22% on the NSN fragment. A comparison of the theoretical and calculated spin densities at N (Table 1) indicates an excellent agreement.

	% s-electron density		% π-electron density		% total spin density	
Atom	DFT	EPR	DFT	EPR	DFT	EPR
N(1)	----	1.7	47.6	44.4	50.7	46.1
S(1)	----	-----	14.2	-----	16.7	-----
C	----	-----	-1.9	-----	-3.1	-----
N(2)	----	0.1	5.6	3.9	5.7	4.0
S(2)	----	-----	9.9	-----	11.1	-----

Table 1. Theoretical spin density distribution determined from DFT calculation and spin density distributions at heterocyclic N atoms from EPR data.

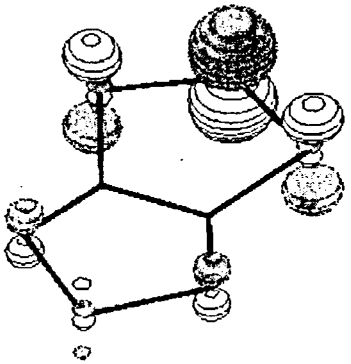

Figure 2: Spin density distribution in the singly occupied molecular orbital of **1**.

CONCLUSION

An excellent agreement is observed between theoretical (DFT) calculations and observed spin density distributions in **1**. We are presently investigating[4] the structure and magnetic behaviour of this radical.

Acknowledgements

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