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Single-Crystal Electron-Spin Resonance Study of the 4-Phenyl-1,2,3,5-dithiadiazolyl Radical*

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Single crystals of 4-phenyl-1,2,3,5-dithiadiazolium trithiatriazinide ($\mathrm{Ph\overline{CNSSN}^{+}S_3N_3^{-}}$), prepared by the reduction of $\mathrm{S_5N_5^{+}AlCl_4^{-}}$ in $\mathrm{SO_2}$ with $\mathrm{(Ph\overline{CNSSN})_2}$, contain a trace paramagnetic impurity which is shown by EPR spectroscopy to be the dithiadiazolyl free radical $\mathrm{Ph\overline{CNSSN}^{\cdot}}$. The g and ^{14}N hyperfine tensors of the radical were deduced from measurements made throughout three mutually orthogonal planes of crystallographically aligned specimens: g = (2.0011, 2.0075, 2.0197); ^{14}N(2) = (37.1, 11.3, 3.4 MHz). Within experimental error, the two nitrogen hyperfine interaction tensors are collinear and have their maximum principal value aligned parallel to g_{min} and perpendicular to the plane of the host cation. The results are interpreted in terms of a planar π-radical which substitutes for the planar host cation, and which has considerable unpaired spin density in N($2p_x$) atomic orbitals directed perpendicular to the heterocyclic ring.

KEY WORDS Electron spin resonance Electron paramagnetic resonance Free radical, π-Radical, Heterocyclic free radical g Tensor Hyperfine interaction tensor Nitrogen hyperfine interaction Dithiadiazolyl Dithiadiazolylium Dithiadiazolium Unpaired electron Unpaired electron spin density

INTRODUCTION

Preliminary studies of free radicals by ESR spectroscopy are almost invariably carried out on dilute liquid or frozen solution samples which cannot provide information on the absolute orientation of **g** or hyperfine tensors.[1] Although such information is not essential for a positive identification, it is often crucial in the assignment of electronic structure.[1–3] It is clearly important, for example, to establish the orientation with respect to the molecular framework of p orbitals contributing to a semioccupied molecular orbital (SOMO) before concluding that the species is a 'π' radical. At best, information obtained from the computer simulation of powder or polycrystalline spectra leads to approximate *relative* orientations of tensors. It is for this reason that single-crystal investigations of the free radical should be undertaken wherever possible in order to confirm the assignments based on liquid and powder spectra. Not that measurements of the latter type should be bypassed: liquid-phase measurements, in particular, provide isotropic parameters which may serve to establish the relative signs of hyperfine tensor components.[1–3]

With very few exceptions, it is generally observed[1–4] that structural similarities between the host matrix and an impurity free radical determine the orientation of the radical within the crystal lattice. As a result, it is possible to transform the principal directions determined for a crystal axis system into an axis system pertinent to the free radical itself. Knowledge of the principal values and directions of both the **g** and **a** tensors in a molecular axis system then allows the determination of the atomic orbital composition of the ground electronic wave function of the free radical.[1–4]

During the early years of ESR spectroscopy, interest in π-electron systems was topical, and many studies were made of so-called cyclic π-radicals.[1] With very few exceptions, that class of free radicals is restricted to carbocycles. However, the growing class of inorganic compounds dubbed[5] 'electron-rich aromatics' offers a potentially fruitful source of novel π-radicals. In particular, a number of ESR studies have been carried out on heterocyclic sulphur–nitrogen free radicals,[6–12] showing certain of them to be remarkably persistent. Of this group, the 1,2,4,3,5-trithiadiazolyl radical, $\mathrm{S_3N_2^{+\cdot}}$, has been shown to be a planar π species with one unpaired electron.[10–13] We have previously examined this radical adventitiously trapped[13] in single crystals of 5-methyl-1,3,2,4-dithiadiazolylium hexafluoroarsenate ($\mathrm{CH_3\overline{CNSNS}^{+}AsF_6^{-}}$). In this work, we have extended our studies to a closely related sulphur–nitrogen–carbon heterocycle, namely the 4-phenyl-1,2,3,5-dithiadiazolyl radical ($\mathrm{Ph\overline{CNSSN}^{\cdot}}$), trapped fortuitously in this instance in single crystals of its cationic equivalent, $\mathrm{Ph\overline{CNSSN}^{+}}$.

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EXPERIMENTAL

4-Phenyl-1,2,3,5-dithiadiazolium trithiatriazinide ($\mathrm{Ph\overline{CNSSN}^+S_3N_3^-}$) was synthesized by reduction of $\mathrm{S_5N_5^+AlCl_4^-}$ in $\mathrm{SO_2}$ by $\mathrm{(Ph\overline{CNSSN})_2}$. Triclinic single crystals, space group $P\bar{1}$,[14] were obtained directly from the reaction mixture.

Good single crystals (about 3–4 mm in length) were selected with the aid of a microscope. They were aligned on a Nonius diffractometer according to the established crystal structure.[14] Such crystals were sealed in the ends of 4 mm quartz tubes with epoxy glue such that each of the three standard[15] orthogonal axes X, Y, Z in turn was aligned along the tube axis. The oriented crystals were positioned in a liquid-nitrogen Dewar vessel or an Oxford Instruments liquid-helium cryostat at the centre of the E-321 microwave cavity of a Varian E-12 EPR spectrometer. The magnetic field intensity was measured with a Bruker ER-035M NMR gaussmeter and the microwave frequency determined using a Systron–Donner digital counter. The axis of the sample tube was held perpendicular to the magnetic field, B_0, of the spectrometer, while a horizontal brass protractor graduated every 5° of arc measured the angle between the magnetic field and a pointer affixed to the sample tube. By rotation of the sample tubes about their axes it was possible to explore each of the three planes XY, XZ and YZ. EPR spectra at 77 K were recorded at intervals of 15° throughout each of these planes. Figure 1 illustrates the dramatic change in the spectrum in the YZ plane as a function of angle.

Absolute spin counts were made by comparison with a crystal[16] of known weight of DPPH (2,2-diphenyl-1-picrylhydrazyl).

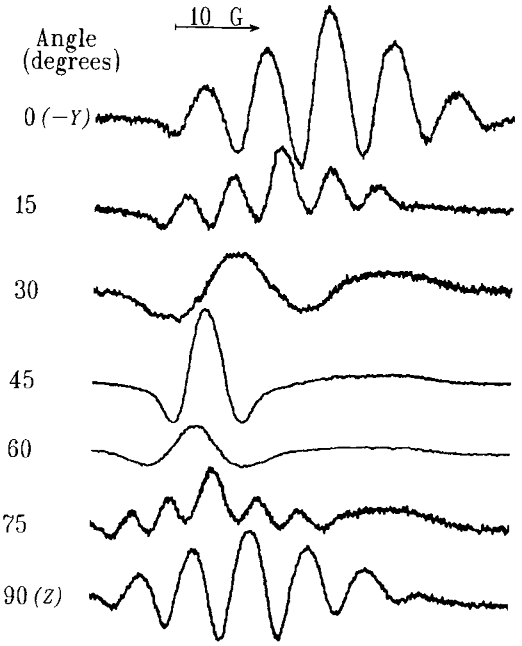

Figure 1 Second-derivative EPR spectra for a single crystal of $\mathrm{[Ph\overline{CNSSN}]^+S_3N_3^-}$ at 77 K as a function of angle in YZ. Magnetic field intensity in units of G (10 G ≡ 1 mT).

RESULTS

For oriented crystals the ESR spectra were found to vary from a single resonance to a well resolved quintet with binomial intensities of 1:2:3:2:1, characteristic of interaction of a single unpaired electron with two equivalent $^{14}\mathrm{N}$ ($I = 1$) nuclei (see Fig. 1). The two hyperfine tensors were evidently collinear, because for no direction within the crystal was there any indication of inequivalence of the two nuclei. This behaviour is similar to that demonstrated in the single crystal ESR examination of the $\mathrm{S_3N_2^{+\cdot}}$ radical.[13]

First-order g and $^{14}\mathrm{N}$ hyperfine couplings were calculated from the spectra as a function of angle within each plane. For each crystal plane the values of g^2 and g^2a^2 were plotted (Fig. 2) against angle, and the best-fit matrix elements for $\mathbf{g}^2$ and $\mathbf{ga}^2\mathbf{g}$ were determined from least-squares computer fits to expressions of the type

$$g^2 = g_{xx}^2 \cos^2 \theta + g_{yy}^2 \sin^2 \theta + g_{xy}^2 \sin 2\theta$$

in order to determine the diagonal and off-diagonal matrix elements (Table 1) which best fit the experimental data (Fig. 2). Since the crystal is triclinic there is no ambiguity in the relative signs of the off-diagonal elements of the two matrices.

Diagonalization of the $\mathbf{g}^2$ matrix gave the principal values and directions of $\mathbf{g}$ (Table 1). The $\mathbf{g}$ matrix was then assembled in the crystallographic axis system. The $\mathbf{a}^2$ matrix was obtained by pre- and post-multiplication of $\mathbf{ga}^2\mathbf{g}$ by $\mathbf{g}^{-1}$, then diagonalized to give principal values and directions of the $^{14}\mathrm{N}$ tensor (Table 1).[4]

The spectrum of an oriented crystal showed no significant change in the temperature range 4–300 K. In particular, no additional spectra were detected throughout that range.

Comparison of the integrated signal intensities from weighed crystals of $\mathrm{Ph\overline{CNSSN}^+S_3N_3^-}$ and DPPH showed that approximately 1% of the former molecular units possessed an unpaired spin.

DISCUSSION

Table 2 compares the principal values and average (isotropic) values of $\mathbf{g}$ and $\mathbf{a}^{\mathrm{N14}}$ obtained from the single-crystal work reported here and the values derived from the powder-spectrum simulations reported elsewhere.[10] The close correspondence between the g values derived from single-crystal and powder samples clearly establishes the identity of the impurity radical in the crystal as $\mathrm{Ph\overline{CNSSN}^{\cdot}}$. The correspondence between hyperfine components is also good for the x direction (maximum interaction), but poor for the other two principal directions. This is almost certainly due to the poor precision of the a_{yy} value derived from simulation of the powder spectrum in perdeuteriotoluene.[10] The simulated spectrum was insensitive to the choice of that particular hyperfine tensor component, and its value was taken to fit the observed isotropic $^{14}\mathrm{N}$ hyperfine interaction. The small hyperfine components obtained from the present single-crystal study are more reliable, although still subject to considerable uncertainty in

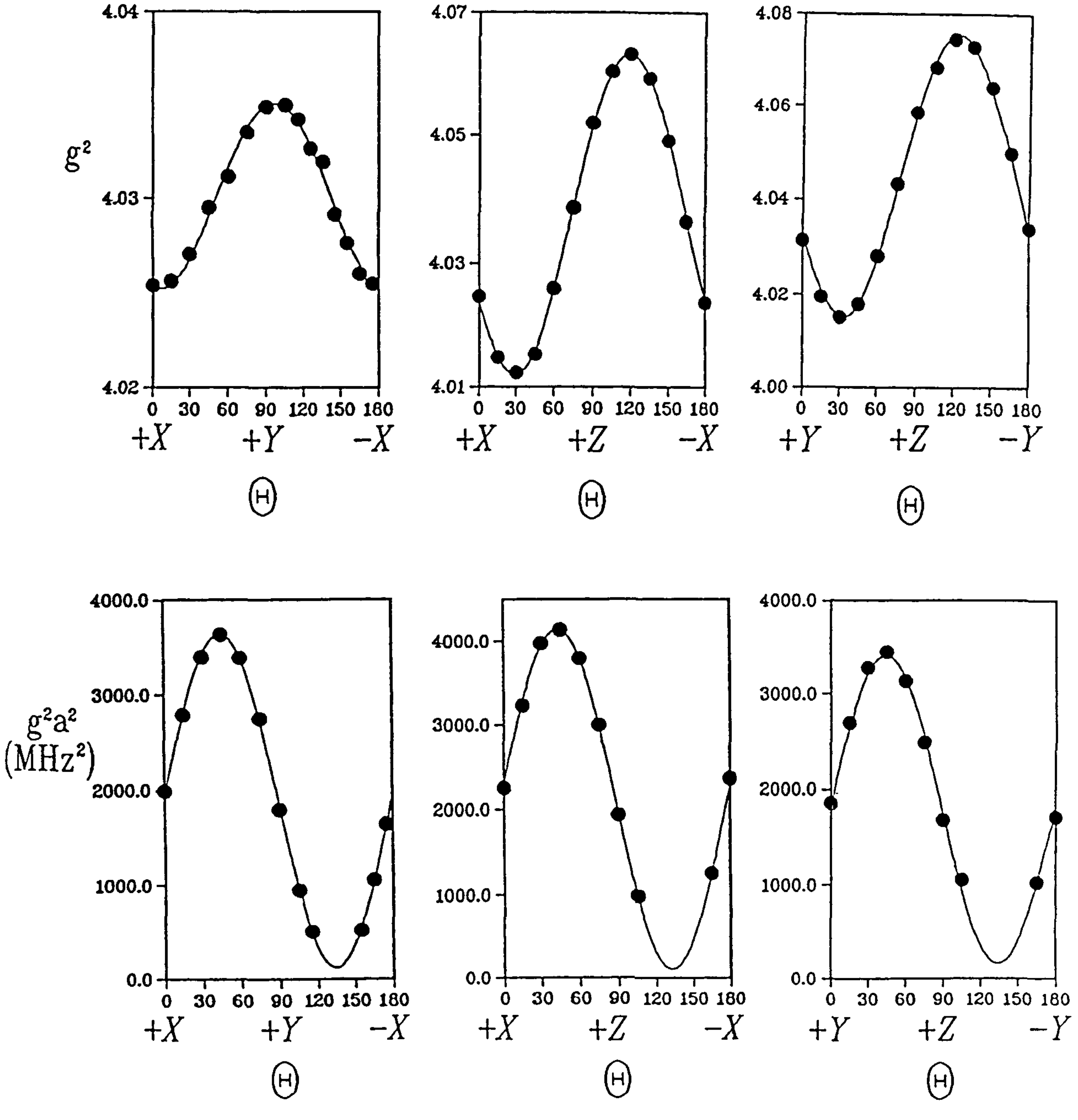

Figure 2. Plots of g^2 and g^2a^2 (MHz^2) for the $\mathrm{Ph\overline{CNSSN}^{\cdot}}$ radical as a function of angle in the three orthogonal crystal planes.

Table 1. The g^2 and hyperfine tensors ga^2g (MHz^2) for the radical $\mathrm{Ph\overline{CNSSN}^{\cdot}}$[a]

	Tensor			Principal values and direction cosines of g, a^{N14}		
	X	*Y*	*Z*	*x*	*y*	*z*
				2.0011	2.0075	2.0197
g^2	4.0241	−0.0011	−0.0216	0.6430	0.7017	−0.3068
	−0.0011	4.0355	−0.0275	0.5187	−0.6937	−0.4997
	−0.0216	−0.0275	4.0542	0.5635	−0.1622	0.8100
				37.10 MHz	11.30 MHz	3.40 MHz
ga^2g ($2^{14}N$)	2090	1590	2018	0.6343	0.5545	−0.5387
	1590	1843	1575	0.5203	−0.8216	−0.2331
	2018	1575	1843	0.5718	0.1324	0.8096

[a] Principal values of **g** and hyperfine interactions in MHz and their direction cosines in the *XYZ* axis system.

Table 2. Comparison of the spectral parameters for PhCNSSN$^{\cdot}$

Matrix	T/K	g_{xx} a_{xx}[a]	g_{yy} a_{yy}	g_{zz} a_{zz}	g_{iso} a_{iso}
PhCNSSN$^{+\cdot}$S$_3$N$_3^-$	77	2.0011	2.0075	2.0197	2.0094[b]
		37.10	11.30	(−)3.40	15.00[b]
Perdeuteriotoluene	109	2.0021	2.0078	2.0218	2.0102
		39.50	3.01	0.99	14.60

[a] Hyperfine interaction in MHz of two equivalent ^{14}N nuclei.
[b] Average of tensor components.

Table 3. Certain unit vectors within the PhCNSSN$^+$S$_3$N$_3^-$ crystal

Direction	Direction cosine X	Direction cosine Y	Direction cosine Z	Angle to g	Angle to a
Perpendicular to ring	−0.5988	−0.5336	−0.5973	3° to g_{min}	2° to a_{max}
Mid-point[a] of S—S to C	−0.3006	−0.5389	0.7869	3° to g_{max}	22° to a_{min}
Cross product	0.7418	−0.6507	−0.1623	3° to g_{int}	23° to a_{int}

[a] *i.e.* The two-fold axis.

view of the line width of *ca.* 8 MHz. In order to match the isotropic parameter[10] as closely as possible, we take the smallest component to be negative (Table 2).

Consideration of the principal directions of the g and ^{14}N hyperfine tensors (Table 3) leaves little doubt as to the location of the free radical within the crystal structure. All three principal directions of g lie parallel within experimental error with certain directions within the host PhCNSSN$^+$ moiety (Table 3) that correspond to the symmetry elements of its pseudo C_{2v} symmetry, namely the two-fold axis, the perpendicular to the ring and their cross-product. Evidently, the dithiadiazolyl free radical has adopted the planar geometry and location of the host cation. A planar ground state is, in fact, expected[11] for the radical. This conclusion is reinforced by the observations for the nitrogen hyperfine tensors: they are collinear and have their maximum component parallel within experimental error to the perpendicular to the ring (Table 3). Because of their near equality and the imprecision in their values, the two small hyperfine components have poorly defined directions. They were found to lie approximately 20° from the other symmetry elements of the host cation.

The situation closely parallels that in the S$_3$N$_2^{+\cdot}$ radical[13] with respect to both principal values and directions of the g and ^{14}N hyperfine tensors. PhCNSSN$^{\cdot}$ and SNSSN$^{+\cdot}$ are clearly analogous 7π-electron heterocyclic free radicals in which the unpaired electron occupies an a_2 antibonding orbital (Fig. 3) which consists primarily of out-of-plane atomic p orbital components from two sulphur and two nitrogen nuclei. S$_3$N$_2^{+\cdot}$ is isoelectronic with the hypothetical species HSiNSSN$^{\cdot}$ and, therefore, pseudoisoelectronic with PhCNSSN$^{\cdot}$. We expect only small, negative spin populations at the ring carbon in PhCNSSN$^{\cdot}$, since as in the case of S$_3$N$_2^{+\cdot}$, symmetry restrictions prohibit direct participation of s or p orbitals from an atom lying on the two-fold axis.[13] The spin population in the nitrogen p$_x$ orbitals is estimated[17] to be significantly higher than in S$_3$N$_2^{+\cdot}$ (24% versus 16% each).

The g shifts for PhCNSSN$^{\cdot}$ are very similar to those observed[13] for the prototypical radical, S$_3$N$_2^+$. Substitution of the unique sulphur by a phenyl-bearing carbon atom evidently causes little change in the disposition of excited states with respect to the $^2A_2$ ground state, and the discussion of spin–orbital interactions given earlier[13] for S$_3$N$_2^{+\cdot}$ is equally applicable here. The smaller displacement of g_{max} from the free-spin value in the phenyl dithiadiazolyl is perhaps a reflection of a lower spin density at the sulphur nuclei in that radical (as suggested by the higher spin density at the nitrogen nuclei).

The present data serve to confirm the inference drawn from earlier powder and solution studies[11] that 4-phenyl-1,2,3,5-dithiadiazolyl is a member of an impor-

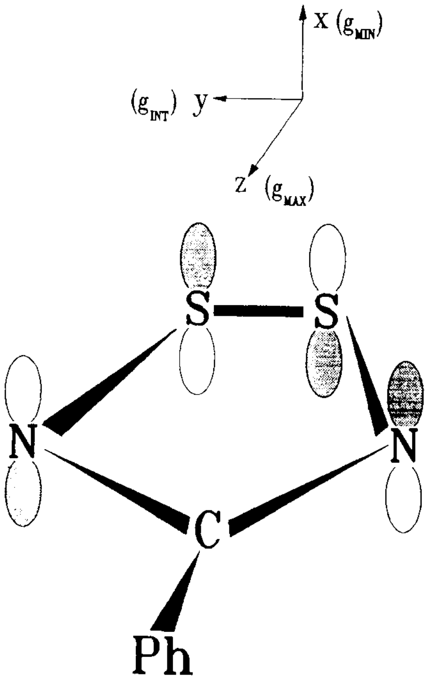

Figure 3. The $^2A_2$ SOMO of 4-phenyl-1,2,3,5-dithiadiazolyl.

tant class of persistent inorganic π-radicals. Its adventitious presence at a level of *ca.* 1% in $\mathrm{Ph\overline{CNSSN}^+S_3N_3^-}$ is not surprising, since a likely impurity from the preparation is the dimer $\mathrm{(Ph\overline{CNSSN})_2}$, which has weak sulphur—sulphur bonds and dissociates readily. We were surprised and disappointed by our failure to detect the $\mathrm{S_3N_3}$ radical either in isolation or as a member of a biradical pair with the dithiadiazolyl. Charge-balance considerations in the lattice dictate that the neutral dithiadiazolyl impurity must be accompanied by a neutral replacement for $\mathrm{S_3N_3^-}$, e.g. a solvent molecule, or by a hole.

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