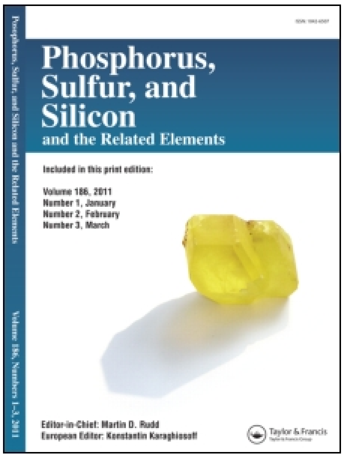

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STRUCTURAL STUDIES OF INORGANIC RING SYSTEMS BY EPR SPECTROSCOPY

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Abstract The power of EPR spectroscopy as a structural probe of free radicals derives from solid-state studies, particularly of single-crystal specimens, that provide detailed information on tensor components and their principal directions. A review of EPR studies of the heterocyclic free radical $S_3N_2^+$ is presented as a guide to the methodology and to illustrate the capabilities of the technique.

INTRODUCTION

The technique of electron paramagnetic resonance (EPR) spectroscopy is unrivalled as a probe of the structure of paramagnetic molecules. Determinations of nuclear hyperfine matrices from measurements on isolated paramagnets often lead to an unequivocal assignment of ground-state geometry and electronic wavefunction, and to a good estimate of the atomic-orbital make-up of the semioccupied molecular orbital (SOMO). The principal values of the electronic Zeeman (g) matrix provide information on the proximity of electronically excited states that can be used in conjunction with MO calculations to corroborate the harder evidence of the hyperfine tensors. Single-crystal measurements on impurity centres in hosts of known structure are particularly informative and structurally definitive. Nowhere is the power of the technique better illustrated than in the chemistry of the five-membered heterocycles collectively known as 7π free radicals[1]. In particular, the 1,2,4,3,5-trithiadiazolyl radical and the pseudo-isoelectronic 4-phenyl-1,2,3,5-dithiadiazolyl radical have been studied in liquid solution, in polycrystalline hosts and as impurity centres in single-crystals. 1,2,4,3,5-trithiadiazolyl is the prototype of a family of persistent heterocyclic free radicals that are under study as spin probes and as precursors to organic metals and magnets[2]. A nearly complete set of EPR parameter matrices is now available[3] for this important species for comparison with theoretical computations. There is a most satisfying correspondence[3-6] between the predictions of simple MO theory and the experimental EPR data that lends credence to the EPR methodology and illustrates its power as a structural probe of paramagnets.

RESULTS AND DISCUSSION

Nuclear hyperfine interaction as a structural probe

The magnetic interactions of an electronic doublet ($S=½$) in a d.c. magnetic field **B** consist[7] of field-dependent electronic and nuclear Zeeman terms together with a number of zero-field terms:

$$\mathcal{H} = \beta \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} + \mathbf{I}\cdot\mathbf{P}\cdot\mathbf{I} - \gamma_n \mathbf{B}\cdot\mathbf{I} \qquad (1)$$

Among the latter, the nuclear hyperfine term (**S·A·I**, for a single nucleus of spin **I**) is normally dominant and the most informative. Like the other EPR parameters in the spin-hamiltonian (1), **A** is a 3x3 matrix (often loosely referred to as a second-rank tensor) that represents the interaction between the single unpaired electron and a magnetic nucleus. Its principal values reflect the extent to which atomic orbitals of the magnetic nucleus participate in the SOMO; its principal directions are determined by the location of the principal axes of participating non-spherical atomic orbitals (*p, d, f*...) in the chosen axis system. All but the isotropic contribution (⅓*Tr***A**) to the hyperfine interaction (hfi) is lost for a freely tumbling radical, so that the spectra of such species provide no direct information on the contributions of *p*, *d* or *f* orbitals. Solid-state spectra are *essential* for the estimation of such contributions. Anisotropic (single-crystal) spectra can provide precise directional information[8,9], relative to molecular axes, that may prove crucial in an electronic ground-state assignment. Unfortunately, the entrapped aligned free radical is uncommon, and the spectroscopist normally has to work with powder spectra in polycrystalline samples or glasses. Such EPR spectra can provide directional information for tensors relative to other tensors, *not* relative to the molecular framework, and only with poor precision. Powder EPR spectra are fraught with pitfalls for the unwary; wherever possible, inferences drawn from their analysis should be substantiated with single-crystal measurements.

With few exceptions, contributions to **A** are dominated by unpaired spin density at the nucleus in question; contributions by through-space dipolar interactions, or by "polarization" mechanisms from unpaired spin density on neighbouring nuclei are usually much smaller, but not entirely negligible[9]. Dipolar interactions are only significant for nuclei with large magnetic moments, such as ^{1}H, ^{31}P or ^{19}F. Spin-polarization contributions to *s* spin density can usually be estimated from the Karplus-Fraenkel relationship[9]. Contributions to **A** from the "unquenched" orbital angular momentum of the unpaired electron are usually unimportant, unless the principal values of **g** depart significantly from the free spin value of 2.0023. Even in such cases, simple corrections proportional to the shifts from free spin, Δg, can be applied[10] to obtain the principal components of the hfi tensor that are due to the intrinsic spin of the unpaired electron. Estimates of the unpaired spin population in atomic orbitals contributing to the SOMO can then be obtained by first separating the isotropic and anisotropic components of **A**, then comparing them with one-electron parameters A_0 and B for the valence-shell atomic orbitals[11]. For the simplest case of a magnetic nucleus that contributes spin densities ρ_s and ρ_p from *s* and p_z orbitals, respectively, to the SOMO, the principal components of the hfi matrix are:

$$\begin{aligned} a_{\parallel} = a_z &= A_0\rho_s + 2B\rho_p \\ a_{\perp} = a_{x,y} &= A_0\rho_s - B\rho_p \end{aligned} \qquad (2)$$

Using these relations, spin densities can readily be obtained from the principal hfi values. In cases where more than one *d* orbital, or where *p* and *d* orbitals from the same nucleus contribute, the estimation of spin densities is more difficult and sometimes equivocal. Because of the relative sizes of A_0 and B, the isotropic component dominates the hyperfine coupling even when $\rho_s \ll \rho_p$. Thus *s*-character has a disproportionate influence on spectral appearance, while substantial *p*- or *d*-character can go unnoticed if linewidths are large, which is often the case in solids. This can result in ambiguity and imprecision in the analysis of powder spectra where the combination of g-anisotropy, small hyperfine anisotropy and a large linewidth can severely limit spectral resolution; it poses less of a problem in single-crystal spectroscopy.

$S_3N_2^+$: a persistent paramagnetic nitrogen sulphide

Figure 1 shows the liquid-phase EPR spectra (^{14}N and ^{15}N) of a persistent free radical frequently encountered when handling cyclic sulphur-nitrogen compounds. The hyperfine manifolds are characteristic of interactions of an unpaired electron with two equivalent nitrogen nuclei, and the chemical provenance strongly suggests the presence of sulphur.

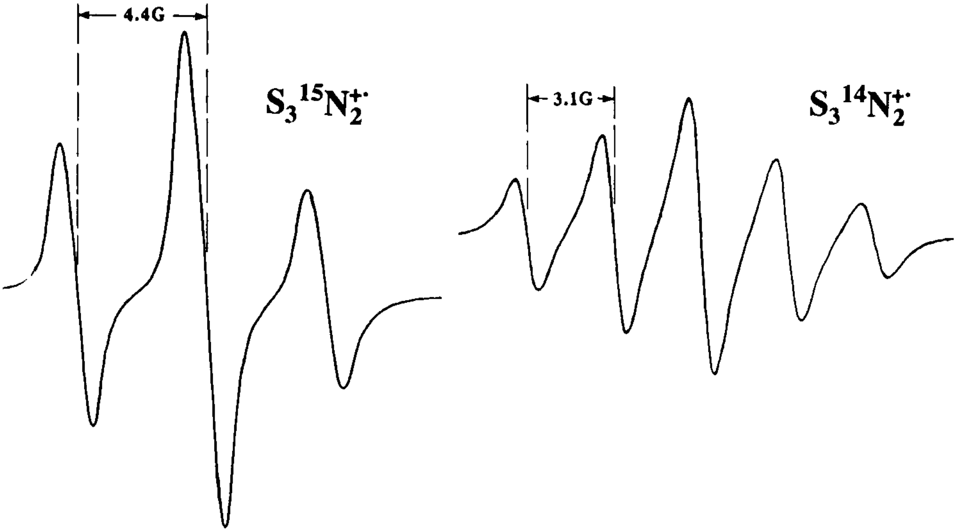

FIGURE 1 1st-derivative EPR spectra of $S_3N_2^+$ in liquid D_2SO_4 at 20°C

Considerations[12] of the powder spectrum and of the ^{33}S satellites in the liquid-phase spectrum arising from natural starting materials led to a rejection of the original assignment of SN_2^+ in favour of $S_2N_2^+$. Subsequently, the same spectrum was observed on dissolution of salts of the $S_6N_4^{++}$ cation in polar solvents[13]. Since the structure of that cation had been established[13] crystallographically as a loosely bound pair of $S_3N_2^+$ radicals, there was a growing suspicion that they were, in fact, the true carrier. Our EPR measurements with doubly enriched (99% ^{15}N, 59% ^{33}S) materials confirmed the presence of a third sulphur atom in the radical[4] and left no further doubts about its identity. By chance, the isotropic ^{33}S hfi of the unique sulphur nucleus was nearly identical to that of the two equivalent ^{14}N nuclei, and had been understandably overlooked in previous analyses of $^{33}S^{14}N$ hyperfine manifolds. An important clue to the electronic structure of this radical was present in the marked linewidth variation across both the sulphur and nitrogen hfi manifolds of the isotropic spectra (Figure 1): large anisotropies were present in both **g** and hfi tensors, indicating substantial N and S valence *p*-orbital contributions to the SOMO. Consideration of the isotropic data for $S_3N_2^+$ leads to the same conclusion, since the total estimated *s*-character is less than 3%, a value consistent with a "π" electronic structure. Applying the Karplus-Fraenkel relationship[9] with recommended values of the constants to the isotropic hfi's, one can estimate populations of 14% 2*p* for each N and 25% 3*p* for each of the two equivalent S. These "guestimates" derived from the liquid-phase spectra turn out to be not too far removed from the orbital populations derived from the measured hfi anisotropies.

Solid-state EPR measurements were required for determination of the full **g**- and hfi tensors, and in the first instance they were made on frozen solutions[3,4]. Fortunately, the powder spectrum of natural $S_3N_2^+$ was free of complications and easy to analyze. **g** was rhombic and $^{14,15}N$ hyperfine coupling was resolved for one principal direction only (Figure 2). Simulations indicated that the **g** and hfi matrices were coaxial to within 20°. However, the frozen spectra of ^{33}S enriched samples were extremely complicated and defied analysis. The problem lay in the overlapping of ^{33}S hfi manifolds for the three canonical directions, and was overcome[3] by resorting to measurements at a higher microwave frequency (Q-band: 34 GHz) where the electronic Zeeman splitting was four times as large (Figure 2). The powder spectrum was further simplified by using 99% enrichment in ^{15}N ($I = \frac{1}{2}$) and by lowering the enrichment in ^{33}S to 30%. In this manner a successful analysis was attained and a full set of hfi tensors derived for all five constituent nuclei together with a nuclear quadrupole interaction tensor for the two equivalent ^{33}S nuclei[3]. The best estimates of the tensor components given in Table I are for the closest match between experimental and computer-simulated spectra under the assumption of coaxial tensors. The powder spectra themselves, unfortunately, provide

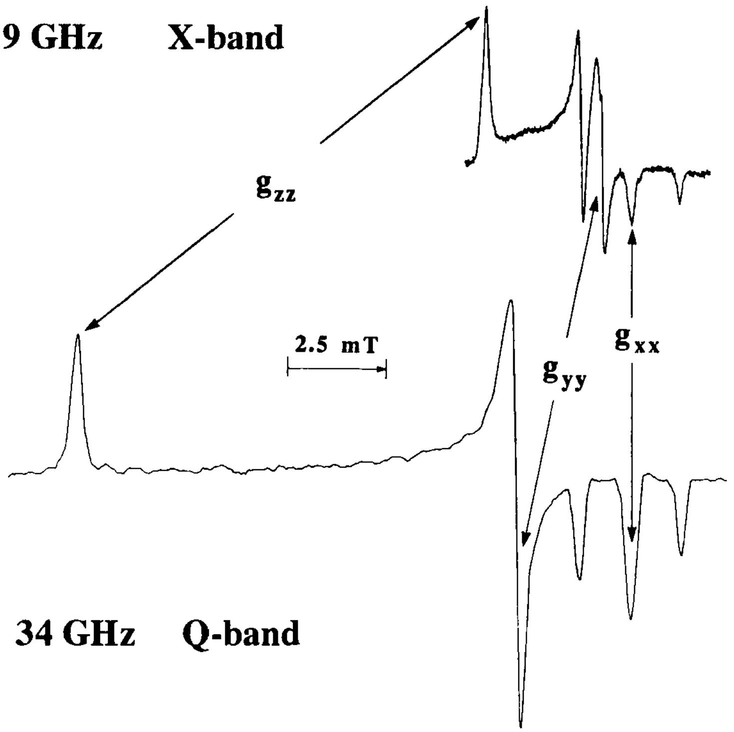

FIGURE 2 1st-derivative X- and Q-band powder spectra of $S_3{}^{15}N_2{}^+$

only a very imprecise check of that assumption. Single-crystal spectra, as we shall see, confirm that g and the nitrogen hfi tensors share a common set of axes that are the symmetry axes of a C_{2v} molecule.

In common with all anisotropic properties of crystals, EPR spectra and parameter matrices derived therefrom are measured with respect to a set of crystal axes. To convert the 3x3 parameter matrices into structurally useful information at the molecular level, one must convert them to a basis of axes of the free-radical impurity centre *via* an orthogonal transformation, *i.e.* a proper rotation[8]. This is normally done by first diagonalizing the matrices in the crystal-axis system to obtain both principal values (eigenvalues) and principal directions (eigenvectors). The latter are then located within the established crystal structure of the host, and are related to the free-radical framework

by assuming that the latter occupies a known orientation within the structure. In the case of substitutional impurity radicals, it is clearly important to use a host very closely related to the guest, so that the assumption of an orientation for the substitutent identical to the displaced host molecule is entirely reasonable. Excellent correlations have been established in this manner for many systems, and give credence to the method[8].

TABLE I **g**, **A**[a] and **P**[b] principal values for $S_3N_2^+$ in D_2SO_4 at 120K

	Component along			
Tensor	*x*	*y*	*z*	Isotropic value
g	2.0013	2.0060	2.0252	2.0111
$^{15}N(2)$	-36.4	<0.5	<0.5	-12.5
$^{33}S(2)$	108.0	-15.0	-17.0	24.2
$^{33}S(1)$	(-)37.0	(+)10.0	(+)2.0	(-)8.4
$e^2Qq_{33}(2)$	±32.0	∓28.0	∓4.0	0.0

[a] hfi components in MHz [b] components of quadrupolar tensor $e^2Qq_{33}(2)$ in MHz

In examining γ-irradiated crystals of 5-methyl-1,3,2,4-dithiadiazolylium hexafluoroarsenate for free-radical products, we detected[5] an anisotropic EPR spectrum that was clearly not the neutral dithiadiazolyl expected from electron addition to the host cation. Consideration of the spectral parameters and examination of unirradiated samples showed that the radical was, in fact, $S_3N_2^+$ that was formed during the preparation of the material from $S_2N^+AsF_6^-$ and CH_3CN, and subsequently entrapped in it in an ordered manner. Crystals were aligned with a Nonius diffractometer according to the known structure of the host, and the crystal planes *ab*, *ac** and *bc** of the monoclinic crystal were explored with the spectrometer. Even before a formal analysis of the data for this crystal, two salient and telling results emerged. Firstly, for *all* directions for which ^{14}N hyperfine structure was resolved, it consisted (for each site) of a quintet of relative intensities (1:2:3:2:1) appropriate for two equivalent nitrogen nuclei. Secondly, the maximum ^{14}N hyperfine coupling and minimum *g*-value both lay close to the *a* crystal axis, which was within 9° of the perpendicular to the host cation plane. If the impurity had, as was most likely, traded places for a host cation, these observations point to a planar π structure for the $S_3N_2^+$ radical. Following transformation of the $\mathbf{g}^2$ and **gAAg** matrices, it was clear that the minimum principal value of **g** (g_{xx} = 2.0021) lay only 1° from the maximum unique principal value of **A** (A_{xx} = 9.1 G) and 6.5° from the host cation plane. The parallel ^{14}N hyperfine tensors were very nearly uniaxial, so that the directions of A_{yy} and A_{zz} were ill-defined; they lay 12° from g_{yy} and g_{zz}, respectively. Since the **g**-tensor was distinctly rhombic, all three of its principal directions were well defined: g_{zz}, the maximum value, lay only 4° from the bisector of the NSN angle of the host, and g_{yy} lay 12° from the CS bond (Figure 3). For the most likely orientation of the impurity cation, *i.e.* in the host plane with all but one of its constituent atoms replacing identical host atoms (Figure 3), those principal directions would be very close to the directions imposed upon **g** by the C_{2v} symmetry of the radical.

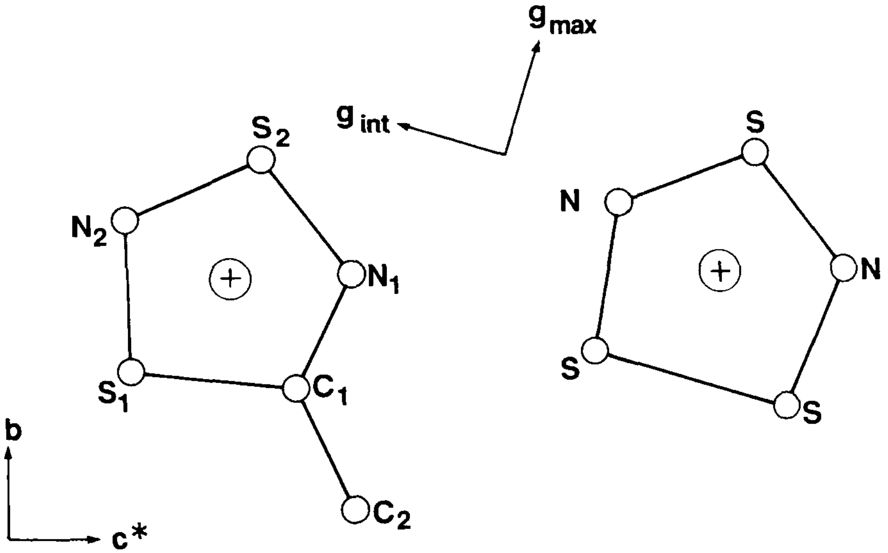

FIGURE 3 Presumed orientation of $S_3N_2^+$ impurity in the host structure

The single-crystal determination thus gives precise information on the angular disposition of three tensors, **g** and the two ^{14}N hfi tensors, with respect to each other. More importantly, for a reasonable assumption of orientation of the free radical in the host structure, it permits the location of the tensor principal directions in the molecular framework. The parallelism of the two ^{14}N hfi tensors, the near perfect alignment of their maximum components with the minimum component of **g**, the proximity of the latter value to that of a free-spin (2.0023), and its location with respect to the molecular plane provide compelling evidence in favour of the inferences drawn from powder spectroscopy: $S_3N_2^+$ has C_{2v} symmetry and is a π radical. In furnishing principal directions within the molecular-axis system, the crystal data also settle the in-plane directions of maximum and intermediate *g*-values (Figure 3).

When a guest free radical and its host are not perfectly matched, nagging doubts always remain concerning the choice of relative orientation. Such was the case for $S_3N_2^+$ in $CH_3\overline{CSNSN}^+AsF_6^-$. Fortunately, serendipity came to the rescue again! In routinely examining crystalline S-N compounds, we happened[14] upon an anisotropic EPR spectrum in single crystals of 4-phenyl-1,2,3,5-dithiadiazolium trithiatriazinide, $Ph\overline{CNSSN}^+S_3N_3^-$. The parameters for the impurity radical were quite distinct from those of $S_3N_2^+$ and corresponded to those of the neutral dithiadiazolyl radical derived from reduction of the host cation. The dithiadiazolyls are a class of 7π free radicals[1] in which the unique S in $S_3N_2^+$ has been replaced by RC^-, and are therefore pseudo-isoelectronic with that species. By exploring crystallographically oriented specimens of the triclinic crystal, we were able to assemble **g** and ^{14}N hyperfine matrices in the usual manner. There were no great surprises. The two ^{14}N hfi tensors were coaxial and their unique principal values lay parallel within experimental error to the minimum principal *g*-value of 2.0011. Assuming identical orientations for the radical and the host cation, it was shown that **g** aligned to within 3° with the symmetry elements of the C_{2v} molecule: g_{max} along the two-fold axis, g_{min} perpendicular to the molecular plane, and g_{int} in that mirror plane along the N-N direction. This finding reinforced the inferences drawn from the crystal study of $S_3N_2^+$, and showed that the dithiadiazolyl radical has an electronic structure very close to that of the prototype.

Simple MO theory at the Hückel level has often been used successfully to predict the electronic ground state and to estimate the unpaired spin densities and relative *g*-shifts in free radicals. For $S_3N_2^+$ in C_{2v} symmetry, Hückel calculations[3-6] suggest a a_2 SOMO not far removed in energy from the b_1 LUMO and approximately 5 eV above a closely spaced pair of doubly occupied b_2 and a_1 levels (Figure 4). The EPR results

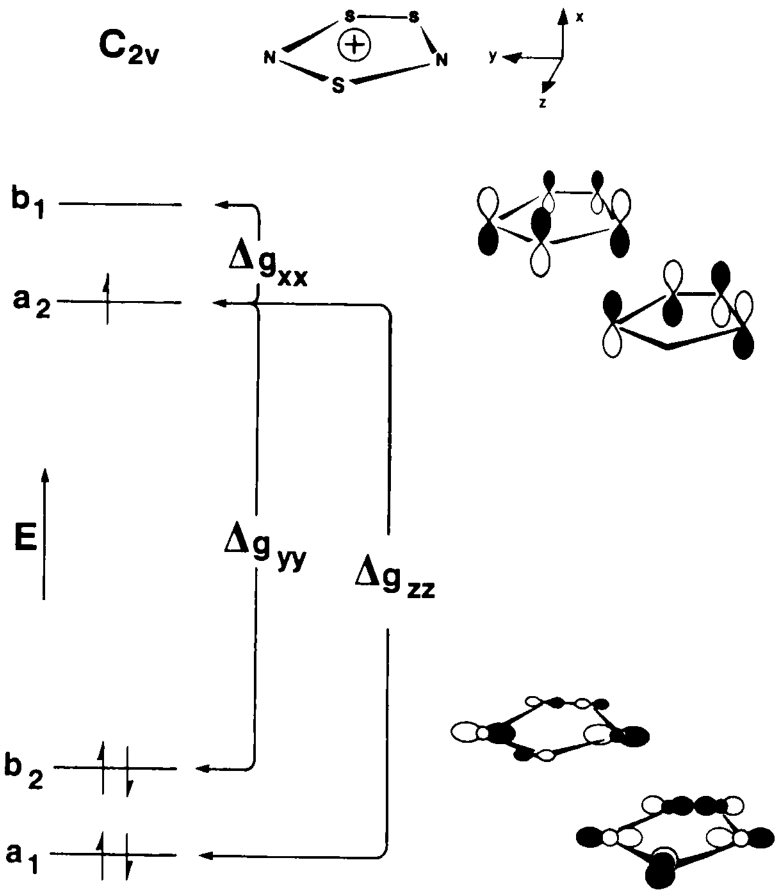

FIGURE 4 Hückel MOs and symmetry-allowed *g*-shifts for $S_3N_2^+$

readily distinguish between the two possible types of π radical in C_{2v} symmetry, $^2A_2$ and $^2B_1$. Unpaired spin populations estimated from the hfi principal components match the expectations for a $^2A_2$ state very well (Table II), but correlate very poorly with those for a $^2B_1$ state. The relative magnitudes of the *g*-shifts along the three principal directions also correlate much better with the values estimated from the Hückel atomic orbital coefficients for the $^2A_2$ ground state than for the $^2B_1$ state. A major difference between the two choices of SOMO lies in the $3p_x$-orbital spin density at the sulfur nuclei (Table II). In a wavefunction of the B_1 representation in C_{2v} symmetry, all five atoms can have

p_x character, but such character is symmetry forbidden for the unique sulfur nucleus in a $^2A_2$ ground state. Although permitted, $3p_x$ unpaired spin density at $S_{1,2}$ in a b_1 SOMO is predicted to be very small compared to that in the a_2 SOMO. Besides the immediate effect on sulfur spin densities and hfi's, this causes a significant reduction in the expected Δg_{zz} for the b_1 choice.

TABLE II Comparison of experimental p_x-spin densities and g-shifts with Hückel-derived estimates

SOMO	nucleus			g-shift		
	$S_{1,2}$	S_4	$N_{3,5}$	Δg_{zz}	Δg_{yy}	Δg_{xx}
a_2	35.6	0.0	14.4	0.025[a]	0.002	0.000
b_1	3.1	43.0	25.4	0.001	0.001	0.000
observed	41.1	(-)14.2	15.6	0.025	0.005	0.000

[a] Calculated g-shift along z set equal to observed value

The a_2 SOMO of $S_3N_2^+$ is antibonding in S-N distance, so that one would expect a drift of unpaired spin away from nitrogen orbitals upon replacing S by Se. At the same time, one would expect a substantial increase in g-shifts because of the much greater spin-orbit coupling parameter of Se *vis-à-vis* that of S. Such trends were indeed observed for the replacement of $S_{1,2}$ by Se atoms[6,15]. Since S_4 orbitals are not implicated in the SOMO, its replacement by a further Se would be expected to have little effect. However, although this substitution caused only minor changes in **g**, it apparently resulted in a substantial increase in the N p-orbital spin density. We have no simple explanation to offer for this observation, except a suspicion that it relates to a marked increase in bond polarizability and bond polarization on substitution by Se. The observation of substantial s and p spin densities, although formally disallowed, at S_4 is an indication of how important such effects may be in this radical.

EPR spectroscopy of $S_3N_2^+$ dilute in liquid, polycrystalline and monocrystalline samples has thus confirmed the identity of the radical and provided a detailed description of its ground-state electronic structure. Simple MO calculations at the Hückel level agree remarkably well with the inferences drawn from experiment.

EXPERIMENTAL

Details of the preparation of materials, of the EPR spectrometer and accessories, and of the experimental procedures are given elsewhere[3-6, 8].

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