# Spin Distributions in Inorganic Heterocyclic Radicals; Generation and E.S.R. Characterization of the 1,3,2,4,6-Thiaphosphatriazinyl $[Ph_2P(Ph)CN_3S]^{\cdot}$

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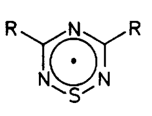
The reaction of $(Me_3SiN)Ph_2PN(Ph)C(NSiMe_3)_2$ with sulphur dichloride affords the 1,3,2,4,6-thiaphosphatriazine $Ph_2P(Ph)CN_3SCl$ which, upon reduction with triphenylantimony, yields the corresponding thiaphosphatriazinyl radical $[Ph_2P(Ph)CN_3S]^{\cdot}$; the e.s.r. spectrum of this radical reveals a spin distribution heavily localized over the (P)–N–S region of the ring.

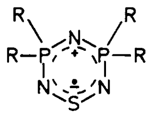
The study of heterocyclic thiazyl radicals, their spin distributions, modes of association, and intermediacy in molecular rearrangements, represents a rapidly growing area of inorganic heterocyclic chemistry.[1] As part of our work in this area we have prepared and characterized radicals based on the 1,2,4,6-thiatriazinyl (**1**)[2,3] and 1,3,5,2,4,6-thiadiphosphatriazinyl (**2**)[4] frameworks. E.s.r. studies indicate that the extensive delocalization of spin density manifested by (**1**) is not found in (**2**). Instead the latter (R = Ph) displays a hyperfine coupling pattern (see Table 1) more reminiscent of those found in acyclic sulphur diimide radical anions $[RNSNR]^{\cdot -}$,[5] suggesting that its electronic structure is more accurately represented by an internal salt formulation. Here we report the preparation and characterization of the novel 1,3,2,4,6-thiaphosphatriazinyl radical $[Ph_2P(Ph)CN_3S]^{\cdot}$ (**3**), a hybrid of (**1**) and (**2**). Analysis of the e.s.r. spectrum of this

**Table 1.** Hyperfine coupling constants[a] *a* (in mT) and MNDO spin densities ρ[b] for (**1**), (**2**), and (**3**).

| Compound position | (1) | | (3) | | (2) | |
|---|---|---|---|---|---|---|
| | *a* | (ρ) | *a*[c] | (ρ) | *a* | (ρ) |
| 1(S) | — | (0.349) | — | (0.429) | — | (0.457) |
| 2(N) | 0.397 | (0.196) | 0.555 | (0.300) | 0.402 | (0.243) |
| 3(C,P) | — | (0.013) | 0.419 | (0.000) | 0.067 | (0.003) |
| 4(N) | 0.397 | (0.171) | 0.111 | (0.099) | 0.000 | (0.003) |
| 5(C,P) | — | (0.013) | — | (0.044) | 0.067 | (0.003) |
| 6(N) | 0.397 | (0.196) | 0.187 | (0.124) | 0.402 | (0.243) |

[a] Data refer to R = Ph. [b] Square of eigenvector coefficients in SOMO. Data refer to R = H. [c] There is also hyperfine coupling to three hydrogens with *a*(H) = 0.035 mT.


(1)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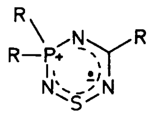
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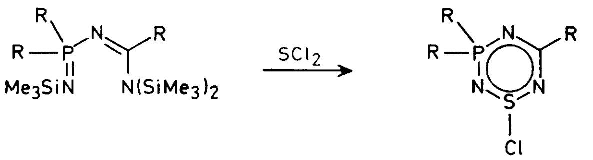
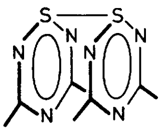


(4) (5)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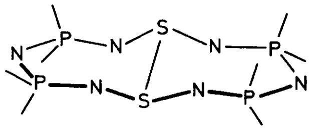
(7)

species allows a comparison of the different spin distributions along the series (**1**), (**2**), and (**3**).

The synthesis of (**3**) requires, as a first step, the reaction (equation 1) of the persilylated phosphimidoylamidine (**4**)[6] (2.6 mmol) with excess of sulphur dichloride (12.6 mmol) in acetonitrile (50 ml), which affords bright yellow crystals of 1-chloro-3,3,5-triphenyl-1,3,2,4,6-thiaphosphatriazine (**5**) in high yield (2.10 mmol, 81%), decomp. >157 °C, δ (P) (ref. $H_3PO_4$) 10.9 p.p.m.

The molecular structure of (**5**) has been determined by *X*-ray diffraction.† An ORTEP drawing of the molecule, along with pertinent structural data for the novel six-membered heterocycle, is shown in Figure 1. Reduction of (**5**) (1.3 mmol) with excess of triphenylantimony (0.85 mmol) in acetonitrile produces an orange/red, powdery (diamagnetic) precipitate with empirical formula $[Ph_2P(Ph)CN_3S]_n$‡ [0.31 g, 68% for (**3**)]. This solid dissolves in methylene chloride to afford an orange solution which exhibits a very strong e.s.r. signal (Figure 2a) characteristic of the thiaphosphatriazinyl radical $[Ph_2P(Ph)CN_3S]^•$ (**3**). The deviation of the *g*-value (2.0057) from the spin-only mark is similar to the effects seen in the related radicals (**1**) and (**2**), and is in keeping with substantial spin density on sulphur. Extraction of hyperfine

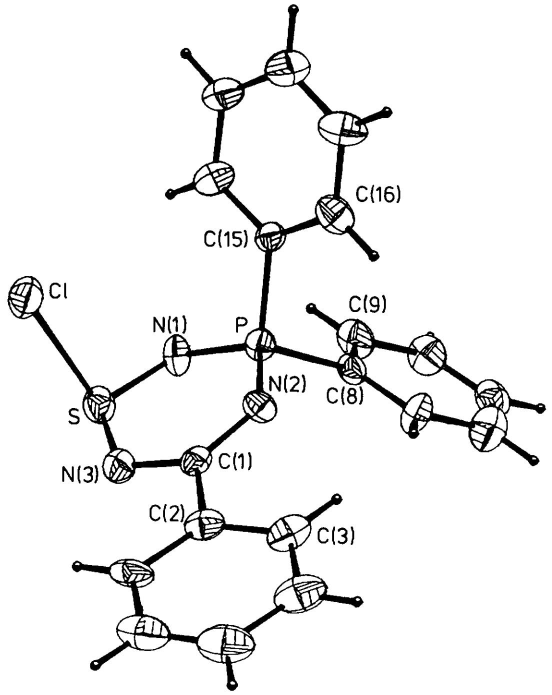

**Figure 1.** ORTEP drawing of $Ph_2P(Ph)CN_3SCl$ (**5**), showing atom numbering scheme. Selected bond lengths and angles are: S–N(1), 1.566(4); N(1)–P, 1.635(4); P–N(2), 1.620(4); N(2)–C(1), 1.311(6); C(1)–N(3), 1.365(6); N(3)–S, 1.561(5); C(1)–C(2), 1.473(8); P–C(8), 1.779(5); P–C(14), 1.784(6); S–Cl, 2.381(2) Å; N(1)–S–N(3), 115.8(3); N(1)–P–N(2), 113.4(2); P–N(2)–C(1), 122.0(4); N(2)–C(1)–N(3), 127.4(5); C(1)–N(3)–S, 121.7(4)°.

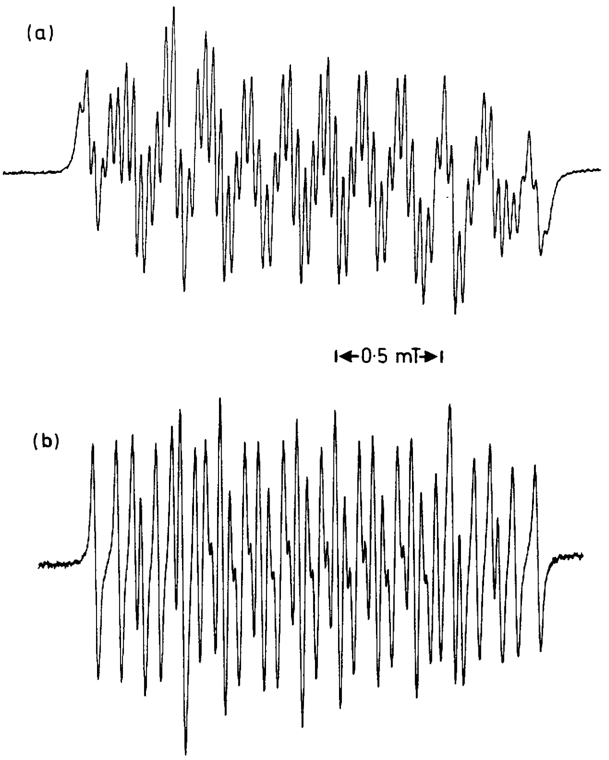

**Figure 2.** (a) E.s.r. spectrum of the 1,3,2,4,6-thiaphosphatriazinyl radical $[Ph_2P(Ph)CN_3S]^•$ (**3**) (in $CH_2Cl_2$ at 22 °C). (b) E.s.r. spectrum of the same radical fully deuteriated ($C_6D_5$) at the 5-position. Hyperfine coupling constants were confirmed by full spectral simulation.

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† *Crystal data* for (**5**): $C_{19}H_{15}PSClN_3$, $M = 383.8$, monoclinic, $P2_1/n$, $a = 8.264(1)$, $b = 14.613(5)$, $c = 15.494(3)$ Å, $\beta = 101.99(1)°$, $U = 1830(1)$ Å$^3$, $Z = 4$, $D_c = 1.39$ g cm$^{-1}$, $\mu = 4.1$ cm$^{-1}$. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$–$2\theta$ scans to $(\sin\theta)/\lambda = 0.48$ Å$^{-1}$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares analysis which minimized $\Sigma W(\Delta F)^2$. 226 Parameters were refined using 983 unique observed reflections [$I > 3\sigma(I)$] to give $R = 0.031$. Reflection intensities decreased more rapidly than average at high $\theta$ values, leading to a less than optimum observation to parameter ratio. However, the final difference maps were clean, and the thermal ellipsoids showed no unusual features. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Satisfactory elemental analyses were obtained for this compound and compound (**5**).

coupling constant data from the spectrum was a non-trivial task. Attempts to obtain ENDOR spectra were successful only for $^{1}H$ nuclei, giving rise to a single doublet (at $-40$ °C) with a coupling constant of 0.035 mT; $^{14}N$ and $^{31}P$ ENDOR spectra were less reproducible. In an attempt to simplify the e.s.r. spectrum, by nullifying the effect of the apparent spin leakage onto the 5-phenyl group, we prepared (starting from $C_6D_5CN$) a sample of (**3**) in which the 5-phenyl group was completely deuteriated. The spectroscopic consequences of this isotopic replacement, illustrated in Figure 2b, are significant, and allow a relatively simple analysis (confirmed by full spectral simulation) of the remaining coupling constants. The $a_P$ and three $a_N$ values are summarized in Table 1, along with relevant data for (**1**) (R = Ph) and (**2**) (R = Ph).

Interpretation of the hyperfine coupling constants for the three radical systems (**1**), (**2**), and (**3**) is aided by comparison with spin densities (square of the SOMO eigenvector coefficients) obtained from (ROHF) MNDO calculations on model systems (with all exocyclic ligands R = H) (Table 1). Accordingly, while replacement of both carbons of (**1**) by phosphorus to give (**2**) effects polarization of spin density towards the NSN unit, substitution of just one carbon, as in (**3**), causes heavy localization of spin density over the (P)–N–S segment, with some delocalization to the other two nitrogens. The $a_P$ value observed in (**3**) is noticeably larger than in (**2**). It is unlikely that this represents a genuine $\pi$-effect; more likely it signals a twisting of the ring (loss of planarity) and consequent leakage of spin density onto phosphorus through the $\sigma$-system. Much larger torsional effects of this type have been observed in more heavily puckered eight-membered rings.[7]

The fate of (**3**) in the solid state has yet to be established. The red/orange diamagnetic solid (which is amorphous to *X*-rays) obtained by the reduction of (**5**) is presumably a dimer but, based on the spin distribution observed, the mode of association is by no means clear. While (**1**) (R = Ph) associates as a simple cofacial adduct with a long sulphur–sulphur bond,[2] *i.e.* (**6**), (**2**) (R = Ph) dimerizes with bond cleavage to produce the twelve-membered macrocycle (**7**).[8] Attempts to isolate compounds related to (**3**) as crystalline dimers are presently underway.

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