Conformational Effects in Inorganic Heterocyclic Radicals; Generation and E.s.r. Characterization of the Thiatriphosphatetrazocinyl Radical $[Ph_6P_3N_4S]^\cdot$

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The reaction of $[Ph_6P_3N_4H_2]^+Cl^-$ with sulphur dichloride affords the eight-membered 1,3,5,7,2,4,6,8-thiatriphosphatetrazocine $Ph_6P_3N_4SCl$, which can be reduced by triphenylantimony to the corresponding thiatriphosphatetrazocinyl radical $[Ph_6P_3N_4S]^\cdot$; the temperature dependence of the e.s.r. spectrum of this radical provides a unique demonstration of the effects of conformational rigidity in an oligophosphazene skeleton.

The chemistry of heterocyclic thiazyl radicals is a subject of current interest.[1] As part of our work in this area we have been concerned about the sharply differing properties of the 1,2,4,6-thiatriazinyl and 1,3,5,2,4,6-thiadiphosphatriazinyl radicals (**1**) and (**2**).[2,3] While the e.s.r. spectrum of (**1**) indicates extensive spin delocalization,[2] that of (**2**) suggests that its electronic structure is best depicted by an ionic formulation.[3] Indeed the hyperfine coupling constant a_N in (**2**) is similar to those found in many acyclic sulphur di-imide radical anions $[RNSNR]^{\cdot -}$.[4] Here we report the preparation and characterization of the 1,3,5,7,2,4,5,8-thiatriphosphatetrazocinyl radical $[Ph_6P_3N_4S]^\cdot$ (**3**), the eight-membered heterocyclic analogue of (**2**). The e.s.r. spectrum of (**3**) substantiates the internal salt formulation for such systems, and illustrates temperature-dependent effects associated with the conformational demands of a larger ring.

The synthetic route to (**3**) involves the reaction of the 1,3,5,2,4,6,7-triphosphatetrazepine hydrochloride (**4**)[5] (4.00 g, 6.12 mmol) with an excess of sulphur dichloride (1.00 g, 9.71 mmol) in acetonitrile. The mixture is heated at reflux under nitrogen for 2 h, then filtered hot to yield a yellow solution, from which the 1,3,5,7,2,4,6,8-thiatriphosphatetrazocine (**5**) crystallizes as pale yellow needles (1.38 g, 2.03 mmol, 33%) decomp. >205 °C, ^{31}P n.m.r. δ ($CDCl_3$; ref. H_3PO_4) 7.9 (2P) and 11.3 (1P). The structure of (**5**) has been confirmed by *X*-ray diffraction.† The ORTEP drawing in

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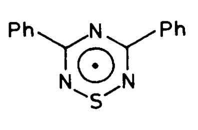
† *Crystal data* for (**5**): $C_{36}H_{30}P_3SClN_4$, M = 679.1, orthorhombic, $P2_12_12_1$, a = 12.028(2), b = 14.836(5), c = 18.759(8) Å, U = 3347 (3) $Å^3$, Z = 4, D_c = 1.35 g cm^{-3}, μ = 3.45 cm^{-1}. Data were collected with an Enraf-Nonius CAD-4 automated diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω–2θ scans to $(\sin\theta)/\lambda$ = 0.53 $Å^{-1}$. No absorption correction was applied. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. 206 Parameters were refined using 1368 unique observed reflections ($I > 3\,\sigma(I)$) to give R = 0.056. 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.



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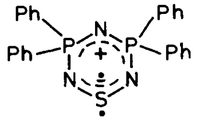

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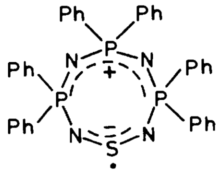

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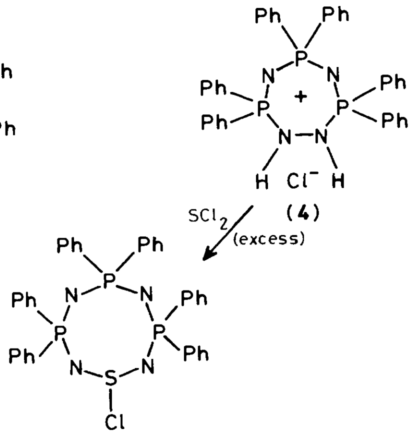

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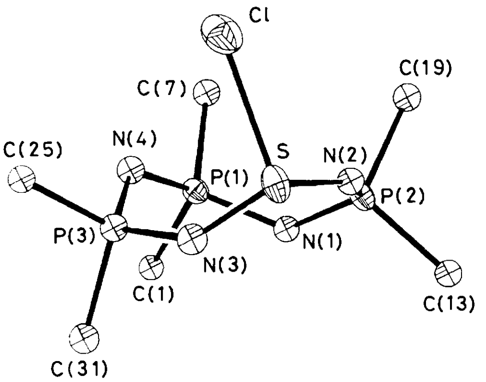

Figure 1. ORTEP drawing of 1-chloro-3,3,5,5,7,7-hexaphenyl-1,3,5,7,2,4,6,8-thiatriphosphatetrazocine (**5**). For clarity only the carbon atoms directly bound to phosphorus are shown. Pertinent bond lengths are S–Cl 2.384(5); S–N(2), 1.545(8); S–N(3) 1.551(8); P(1)–N(1), 1.593(8); P(1)–N(4), 1.594(8); P(2)–N(1), 1.573(8); P(2)–N(2), 1.632(7); P(3)–N(3), 1.623(8); P(3)–N(4), 1.590(8) Å. Endocyclic angles (°) are S 117.7(5); P(1) 118.0(4); P(2) 121.5(4); P(3) 118.9(4); N(1) 133.1(5); N(2) 138.4(5); N(3) 135.2(6); N(4) 126.3(5)°.

Figure 1 illustrates the structure of the P_3N_4S ring, which adopts a boatlike conformation [distances of endocyclic atoms from mean molecular plane: P(1) +0.153(3); N(1) −0.505(8); P(2) −0.030(3); N(2) +0.251(8); S +0.301(3); N(3) −0.465(9); P(3) −0.268(3); N(4) +0.564(8) Å] reminiscent of those seen in sterically crowded tetrameric cyclophosphazenes.[6] The local geometry about sulphur is similar to that observed in $Ph_4P_2N_3SCl$.[7]

Reduction of (**5**) in toluene with triphenylantimony generates a bright orange solution which exhibits a strong e.s.r. signal (g = 2.0064) characteristic of (**3**) (Figure 2). The hyperfine coupling constants to nitrogen (a_N = 0.78 mT) are slightly larger than in (**2**) (a_N = 0.402 mT), but those to phosphorus (a_P = 2.45 mT) are much larger [a_P = 0.067 mT in (**2**)].[3] We believe these differences can be attributed to the expected [on the basis of (**5**)] non-planarity of the P–NSN–P unit in (**3**), which allows spin density from the pseudo sulphur di-imide radical anion, formally a π-radical, to 'leak' into *s*-type orbitals on both nitrogen and phosphorus, thereby drastically increasing the Fermi contact interactions at these atoms. In short, hyperfine coupling constants serve as very sensitive probes of molecular conformation.

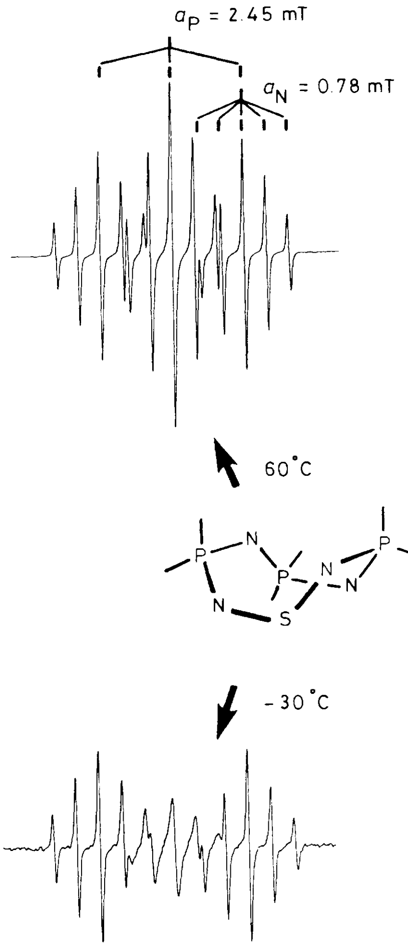

Figure 2. E.s.r. spectrum of 3,3,5,5,7,7-hexaphenyl-1,3,5,7,2,4,6,8-thiatriphosphatetrazocinyl (**3**) in toluene at +60 °C and −30 °C; coupling constants taken from the high-temperature limiting spectrum.

The e.s.r. spectrum of (**3**) is temperature-dependent. A sharp triplet of quintets with a 1:2:1 intensity pattern is observed only at elevated (> 60 °C) temperatures. At lower temperatures the central quintet broadens and eventually collapses into the base-line near −50 °C. We interpret these changes in terms of the freezing out of conformational motion in (**3**), an effect which forces a non-equivalence of the two ends of the P–NSN–P unit. Below −60 °C the signal of (**3**) disappears, presumably as a result of radical association. In the absence of spectral data for the slow exchange limit we have been unable to gain any quantitative insight into the rate of conformational tumbling. Nonetheless this classic example of an alternating linewidth effect[8] represents, to our knowledge, the first observation of conformational rigidity in a phosphazene-based ring system.

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