The Synthesis and X-Ray Structural Characterisation of an Unusual Seven-membered Diaza-phospha-tetrathia Heterocycle

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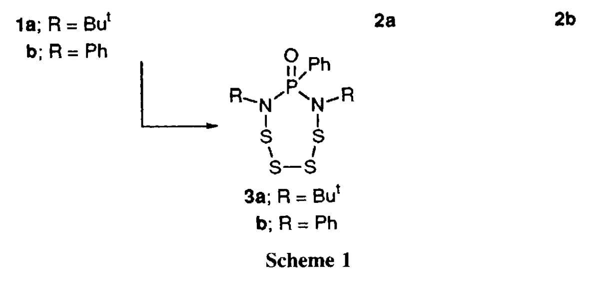
When the di-aryl or di-alkyl phenyl phosphonamide $(RNH)_2P(O)Ph$ **1** is treated with sulfur(I) chloride (S_2Cl_2) in base, the product is an unexpected, unusual seven-membered diazatetrathiaphospha heterocycle **3**; the X-ray structure and NMR spectra of these two unique heterocycles indicate that they exist in a pseudo-chair conformation with steric congestion limiting the freedom of rotation of the phenyl group; and represent the first known examples of this hetero-ring system.

Close-proximity diradical species may have importance in the field of non-metallic magnetic materials. Such radicals that do not bond, if generated in large enough arrays, might have unusual magnetic properties.[1] In an attempt to synthesise proximate bis-thionitroxides **2b**, sulfur(I) chloride was treated with the phosphonic diamides **1**.† It is known that secondary amines upon treatment with S_2Cl_2 produce bis(disubstituted amino) disulfides, which in turn generate thionitroxides at elevated temperatures or under photolysis conditions.[2] However, in this instance instead of the expected five-membered ring bis(thionitroxide) precursor **2a**, elemental sulfur and an unusual seven-membered ring system **3** containing a chain of four sulfur atoms were the only isolable products (Scheme 1).

Single crystal X-ray analysis (Figs. 1 and 2) indicates that both **3a** and **3b** show a preference for a pseudo-chair conformation with two non-equivalent R groups. The situation is similar in solution, at least for **3a**, where the NMR[3] (^1H and ^{13}C) demonstrate the *tert*-butyl groups are present in different environments (essentially axial or equatorial with respect to the pseudo-chair). The two sharp singlets (from the magnetically non-equivalent *tert*-butyl groups) remain unchanged at −50 to +90 °C. Also, in the ^1H NMR of **3a** the two *ortho* protons (of the phenyl ring bound to the phosphorus) display non-equivalence (at < 0 °C) and remain broadened until quite high temperatures (> 60 °C). Clearly the phenyl ring is restricted in its rotation and hence these two hydrogens remain in non-equivalent environments (on the NMR timescale). These results imply that this novel P–N–S ring system possesses a high conformational rigidity. The nitrogen lies in a planar environment and therefore has much sp^2 character, presumably because of pπ–dπ overlap with the phosphorus atom. The high conformational rigidity of **3a** may be a result of restricted P–N bond rotation and steric congestion between the two *tert*-butyl groups and the phenyl ring in the transition state necessary for 'ring inversion'. The N–S bond lengths are very close to those of other N–S ring systems involving single bonds[4] indicating only σ bonding.

The crystal structure of **3b** shows a remarkable similarity to that of **3a**, despite the differing steric demands of the *tert*-butyl and phenyl groups. The *ortho* hydrogens of the phenyl ring bound to phosphorus display the same broadening as evidenced with **3a**, and there is little effect on the P–N bond distances (all are very close to 1.69 Å in both structures). This is not surprising as the *N*-phenyl rings, at least in the solid state, are twisted from the P–N–C plane, thereby decreasing the pπ–pπ overlap.



Scheme 1

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† *Synthesis and spectroscopic data*: the phosphonic diamide **1** was prepared according to the literature procedure of Quast.[6] To synthesise **3a** a solution of **1** (200 mg, 0.75 mmol) in dry pyridine (5 ml) was cooled to 0 °C under an inert atmosphere and S_2Cl_2 (220 mg, 1.6 mmol) was added slowly with stirring *via* a syringe. Work-up followed by flash silica chromatography and reversed phase HPLC gave **3a** (75 mg, 25.4%, m.p. = 123–125 °C from $CHCl_3$). ^1H NMR ($CDCl_3$: δ 1.35 (s, 9H, *tert*-butyl), 1.71 (s, 9H, *tert*-butyl), 7.42–7.52 (m, 3H, ArH) and 8.05 (vbrs, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 29.7 (s, 3 × CH_3), 30.7 (s, 3 × CH_3), 62.8 (d, *C*Me_3), 66.2 (d, *C*Me_3), 127.5 (vbrs, ArC), 131.1 (s, ArC), 132.2 (vbrs, ArC), 135.5 (vbrs, ArC), 136.1 (d, ArC). Doublets (d) indicate coupling to phosphorus, very broad singlets (vbrs) indicate non-homogeneity. ^{31}P NMR showed only one peak. Mass spectrometry using EI and CI (ammonia) gave no clear molecular ion.

A similar procedure gave **3b** (24%), m.p. = 163–164 °C (acetonitrile). ^1H NMR ($CDCl_3$): δ 7.2 (vbrs, ArH), 7.3–7.4 (m, ArH), 7.5 (d, ArH), 7.8 (dd, ArH). ^{13}C NMR ($CDCl_3$): d 127.4 (brs, ArC), 127.9 (s, ArC), 128.0 (vbrs, ArC), 128.1 (s, ArC), 129.1 (s, ArC), 132.2 (d, ArC), 132.7 (s, ArC), 132.8 (s, ArC). ^{31}P NMR showed only one peak. Mass spectrometry using CI (methane) gave a molecular ion at 435 ($C_{18}H_{15}N_2OPS_4$ + 1).

Crystal data for: **3a** $C_{14}H_{23}N_2OPS_4$, $M = 394.6$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.461(4)$, $b = 14.399(1)$, $c = 12.854(5)$ Å, $\beta = 93.29(2)°$, $U = 1933(1)$ Å^3, $D_c = 1.355$ g cm^{-3}, Mo-Kα radiation $\lambda = 0.71073$ Å, μ (Mo-Kα) = 5.6 cm^{-1}, $F(000) = 832$, T 297 K.

3b $C_{18}H_{15}N_2OPS_4$, $M = 434.5$ monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.386(6)$, $b = 8.884(1)$, $c = 15.520(6)$ Å, $\beta = 100.88(2)°$, $U = 1948(1)$ Å^3, $D_c = 1.482$ g cm^{-3}, Mo-Kα radiation $\lambda = 0.71073$ Å, μ (Mo-Kα) = 5.8 cm^{-1}, $F(000) = 896$, T 297 K.

Appropriate crystals (0.18 × 0.35 × 0.12 mm for **3a** and 0.12 × 0.25 × 0.02 mm for **3b**) were cleaved from larger elongated plates. Data sets consisting of 3765 and 3827 reflections ($2\theta_{max} = 50°$) were collected on an Enraf-Nonius CAD-4 diffractometer using graphite crystal monochromatized Mo-Kα X-radiation. Data were corrected for Lorentz and polarization effects and for absorption (empirical methods). The structures were solved by direct methods (SHELXS-86[7]) and refined by least-squares analysis using SHELX-76.[8] Residuals R $[= \Sigma||F_o| - |F_c||/\Sigma|F_o|]$ and R_w $[= \Sigma\, w(|F_o| - |F_c||^2/\Sigma w\, |F_o|^2)^{0.5}]$ of 0.0307 and 0.0356 **3a** and 0.0849 and 0.0854 **3b** were obtained using 2425 and 1582 reflections respectively $[I > 2.5\sigma(I)]$. Values for A of 1.15×10^{-3} and 1.55×10^{-2} in the weighting equation $w = [\sigma^2(F_o) + A(F_o)^2]^{-1}$ were used. Anisotropic thermal parameters were used for all non-hydrogen atoms. Most hydrogen atoms were located in difference-Fourier analyses and included with coordinates refined but with isotropic U values fixed at 0.05 Å^2. Some disorder in one of the phenyl rings (for **3b**) meant that the hydrogens could not be located so were included at calculated positions. This disorder is considered responsible for the higher residual for the compound **3b**. Neutral atom scattering factors and values for f', f'' terms for anomalous dispersion were taken from the International Tables for Crystallography.[9]

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

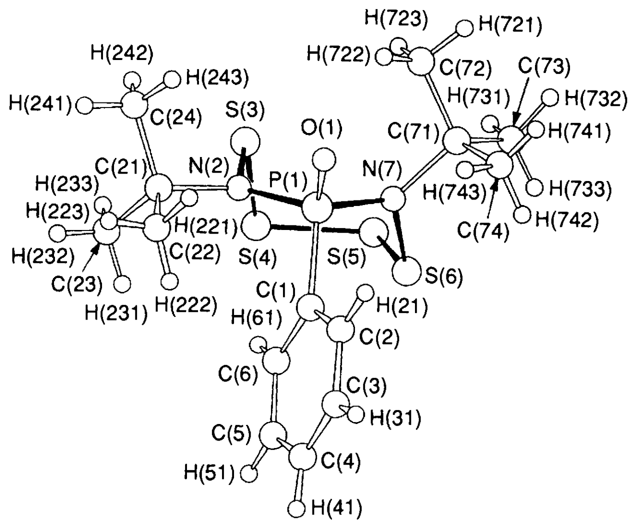

Fig. 1 Molecular configuration and naming scheme for compound **3a**. Bond lengths and angles of significance lie about each of the similar nitrogen atoms N(2) and N(7). These comparative distances (Å) and angles(°) for (**3a**) and (**3b**) (Fig. 2) are respectively: N(2)–P(1) 1.688(2), 1.678(9); N(2)–S(3) 1.686(2), 1.710(8); N(2)–C(21) 1.538(3), 1.445(14); N(7)–P(1) 1.691(2), 1.686(9); N(7)–S(6) 1.684(2), 1.698(9); N(7)–C(71) 1.533(3), 1.442(13); S(3)–N(2)–P(1) 121.3(1), 120.7(5); C(21)–N(2)–P(1) 122.0(2), 121.1(6); S(3)–N(2)–C(21) 114.3(2), 114.3(7); S(6)–N(7)–P(1) 115.9(1), 120.8(5); C(71)–N(7)–P(1) 122.3(2), 120.6(7); and S(6)–N(7)–C(71) 120.1(2), 118.0(7).

The mechanism of formation of **3** remains unclear. It is possible that **3** is formed *via* the expected disulfide (**2a**). This species might be in equilibrium with the bis(thionitroxide) **2b** which could then react further with S_2Cl_2. Such a process should result in the formation of chlorine gas, which was not apparent. In addition when the reaction was undertaken in the presence of methyl acrylate the production of **3** was unaffected. However, thionitroxides have been reported to be reluctant to add to alkenes,[5] so this result cannot be taken as definitive evidence for the absence of this species.

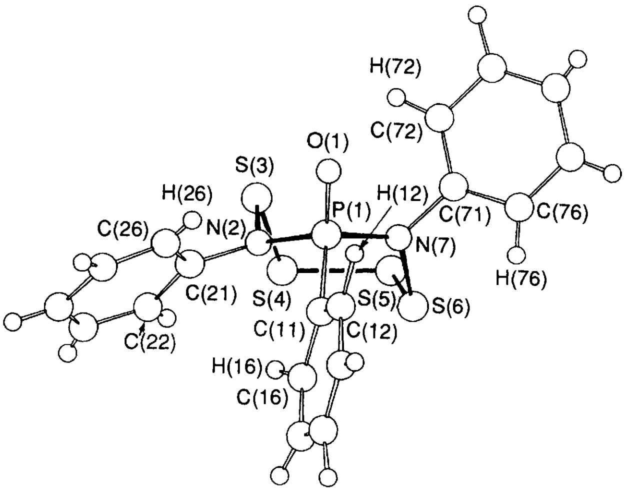

Fig. 2 Molecular configuration and naming scheme for compound **3b**

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