Preparation and X-Ray Structure of a New Organo-P–O–S Heterocycle

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Reaction of 1,3-epithio-$1\lambda^5,3\lambda^5$-naphtho[1,8-*cd*][1,2,6]thiadiphosphinine-1,3-dithione **5** with 3,5-di-*tert*-butylcatechol gives 3,5-di-*tert*-butyl-1,8-epithio-$1\lambda^5,8\lambda^5$-naphtho[1,8-*cd*][1,7,2,6]benzodioxadiphosphonine-1,8-dithione **7** which, from X-ray studies, contains fused C_3P_2S and $C_2O_2P_2S$ rings.

The heterocyclic chemistry of phosphorus systems is of great significance but not as well studied as that of lighter elements. Along with other aspects there is significant interest in the use of phosphorus–sulfur reagents for organic transformations. Recently, there have been some reports on ring-forming reactions. The reaction of Lawesson's reagent $(MeOC_6H_4P)(S)S_2P(S)(C_6H_4OMe)$ **1** (Fig. 1) with compounds containing a pair of hydroxy groups has been described.[1,2] These types of reactions provide simple routes to compounds containing C–O–P and C–O–P–S rings. Thus, reaction of **1** with catechol yields 2-(4-methoxyphenyl)-1,3,$2\lambda^5$-benzodioxaphosphole-2-thione[1] **2**, whereas with ethane-1,2-diols, 4,5-dihydro-1,3,$2\lambda^5$-dioxaphosphole-2-thione **3** together with 2,4-bis(4-methoxyphenyl)-6,7-dihydro-1,5,3,$2\lambda^5$,$4\lambda^5$-dioxathiadiphosphepine-2,4-dithione **4** are obtained (from spectroscopic studies). We have previously reported[3] on the preparation of 1,3-epithio-$1\lambda^5,3\lambda^5$-naphtho[1,8-*cd*][1,2,6]thiadiphosphinine-1,3-dithione **5** and have investigated its reaction with alcohols[4] and more recently with ethane-1,2-diol[5] to give 1,3-bis(2-hydroxyethoxy)-$1\lambda^5,3\lambda^5$-naphtho[1,8-*cd*][1,2,6]thiadiphosphinine-1,3-dithione **6**. Here we describe the synthesis and full characterisation of a new organo-P–O–S ring system 3,5-di-*tert*-butyl-1,8-epithio-$1\lambda^5,8\lambda^5$-naphtho[1,8-*cd*][1,7,2,6]benzodioxadiphosphonine-1,8-dithione **7** from the reaction of **5** with 3,5-di-*tert*-butylcatechol.

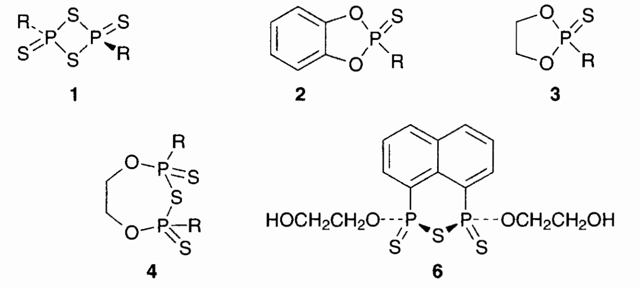
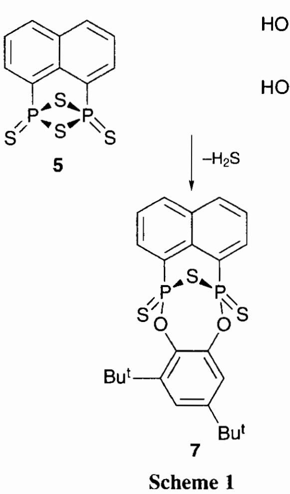


Fig. 1 Examples of P–S and organo-P–S heterocycles (R = *p*-MeO-C_6H_4). Compounds **2**–**4** are proposed on the basis of spectroscopic evidence,[1,2] whilst **5** has been crystallographically characterised.



Scheme 1

Thus, **5** (0.51 g, 1.6 mmol) and 3,5-di-*tert*-butylcatechol (0.705 g, 3.2 mmol) were heated in refluxing toluene (20 ml) under nitrogen for 5 days. On cooling, the product was obtained as a white solid (0.25 g, 0.495 mmol, 31%). MS and NMR (^{31}P and ^1H) indicated that the reaction had proceeded according to Scheme 1. The $^{31}P\{^1H\}$ NMR spectrum is an AX system [δ_A 74.4, δ_X 71.2, J (^{31}P–^{31}P) 3.2 Hz]. A crystal suitable for X-ray studies was obtained from dichloromethane solution.

The X-ray structure† of **7** reveals two independent molecules which are not significantly different from each other. The structure consists of fused naphthyl P_2S (C_3P_2S) and aryl O_2P_2S ($C_2O_2P_2S$) rings. There are very few reports of X-ray characterisation of the C_3P_2S ring and, to our knowledge, no reports on the $C_2O_2P_2S$ ring. The napthyl P_2S ring is close to planar with P(1) and P(9) 0.29 (0.33) and 0.26 (0.40 Å) above and below the mean plane respectively (values in parentheses are for the equivalent distances in the second independent molecule). The

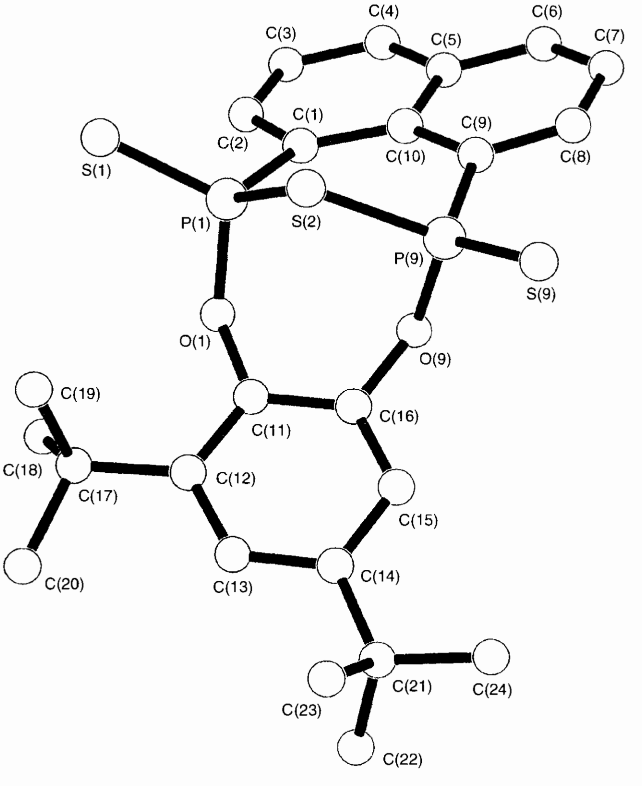


Fig. 2 The X-ray structure of one of the independent molecules in **7**. Selected bond lengths (Å) and angles (°) [equivalent parameters for the second independent molecular are in square brackets]: P(1)–S(1) 1.917(2) [1.917(2)], P(1)–S(2) 2.074(2) [2.082(2)], P(9)–S(9) 1.905(2) [1.902(2)], P(9)–S(2) 2.087(2) [2.088(2)], P(1)–(O) 1.606(3) [1.607(3)], P(1)–C(1) 1.817(4) [1.809(4)], P(9)–O(9) 1.607(3) [1.614(3)] P(9)–C(9) 1.783(4) [1.780(4)], C(11)–O(1) 1.407(4) [1.403(4)], C(16)–O(9) 1.409(4) [1.410(4)], P(1)–S(2)–P(9) 97.21(6) [96.97(6)], S(1)–P(1)–S(2) 109.90(8) [109.83(8)] S(1)–P(1)–C(1) 113.2(1) [113.4(1)], S(1)–P(1)–O(1) 112.1(1) [111.9(1)], S(2)–P(1)–O(1) 106.5(1) [106.6(1)], S(2)–P(9)–S(9) 110.51(8) [111.38(7)], S(9)–P(9)–C(9) 119.1(1) [118.5(1)], S(9)–P(9)–O(9) 117.5(1) [118.1(1)], P(1)–O(1)–C(11) 130.0(2) [129.8(2)], P(9)–O(9)–C(16) 120.3(2) [119.5(2)], O(1)–P(1)–C(1) 106.9(2) [106.6(2)], O(9)–P(9)–C(9) 98.0(2) [98.2(2)].

bridging sulfur lies close to the P_2 naphthyl mean plane 0.07 (0.29 Å) whilst the exocyclic sulfur atoms lie below the plane with the two oxygen atoms lying above this plane and the O(1)–C(11)–C(16)–O(9) group (which is essentially planar) being inclined by *ca.* 31° (34°).

As expected, the exocyclic P=S bond lengths are significantly shorter than those to the bridging sulfur. The P–O bond lengths [range 1.606(3)–1.614(3) Å] and C–O bond lengths [range 1.407(4)–1.410(4) Å] are effectively single bond in character. The phosphorus atoms have distorted tetrahedral geometry whilst the bridging sulfur angle 97.21(6)° [96.97(6)°] is reduced and the P–O–C angles are approximately trigonal [range 119.5(2)–130.0(2)°]. The molecules pack with partial face-to-face overlap of the naphthyl rings to form stacks along the *c* axis (Fig. 2). The naphthyl–naphthyl separation is 3.4 Å.

The structure here may offer some insights into mechanisms of reactivity that are available for P–S compounds such as Lawesson's reagent with organic substrates. Clearly, in this case the reaction proceeds *via* nucleophilic attack of a catechol oxygen atom at a phosphorus centre followed by ring closure. The fact that ring closure across both phosphorus atoms is observed is in contrast to the analogous reaction with Lawesson's reagent and indicates that **2** is not well represented as dissociating into two *cis* RPS_2 groups. The difference in reactivity between catechol and alkyl diols is probably a consequence of the pre-organisation associated with the catechol system. The usefulness of **2** in ring forming reactions has been demonstrated.

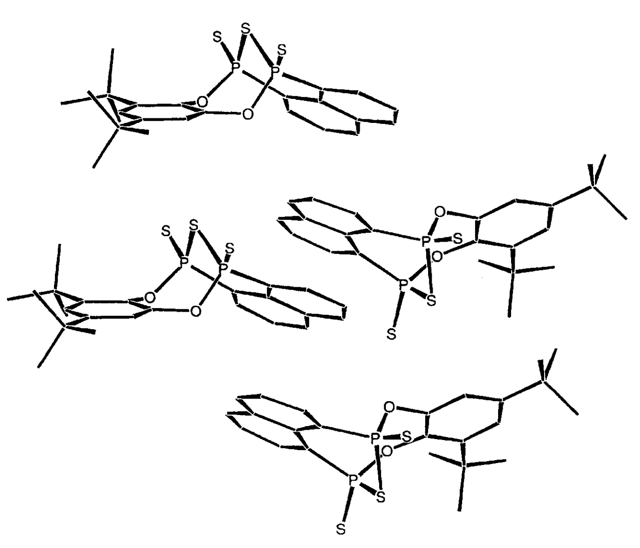


Fig. 3 View of the stacking along the *c* axis in the structure of **7**

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Footnote

† *Crystal Data* for **7**: $C_{24}H_{26}O_2P_2S_3$, M = 504.6, triclinic, space group $P\bar{1}$, a = 18.851(2), b = 20.032(3), c = 6.7032(5) Å, α = 92.686(9)°, β = 94.790(8)°, γ = 92.76(1)°, U = 2516 Å^3, Z = 4, T = 292 K, D_c = 1.33 g cm^{-3}, $F(000)$ = 1056, λ = 1.54178 Å, μ(Cu-Kα) 4.05 mm^{-1}, Rigaku AFC 7S diffractometer, ω-scans ($2\theta_{max}$ = 120°). Crystal dimensions 0.12 × 0.12 × 0.51 mm. Of 7303 measured data 7037 were unique (R_{int} = 0.025) and 5036 were observed [$I > 3.0\sigma(I)$]. An absorption correction based on azimuthal scans was applied. The structure was solved by direct methods and refined to give R = 0.041 and R_w = 0.041.

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

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