Reactions of 1,3-Epithionaphtho[1,8-*cd*][1,2λ⁵,6λ⁵]thiadiphosphinine-1,3-dithione; the Preparation and X-ray Structure of NpP(S)(SMe)SP(S)(OMe), the first C_3P_2S Ring

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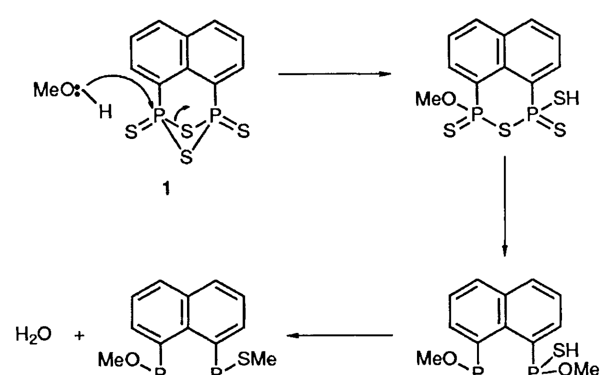
NpP_2S_4 **1** (Np = $C_{10}H_6$, naphthalene-1,8-diyl) reacts with carbonyl groups to give thiocarbonyls whilst refluxing **1** in methanol results in cleavage of one of the P–S–P bridges and formation of the new heterocycle **3** which contains a C_3P_2S ring with the phosphorus atoms asymmetrically substituted by methoxy and thiomethoxy groups.

Recently, we reported[1] that reaction of bromonaphthalene with P_4S_{10} gives **1**, a relative of the widely used Lawesson's reagent **2**.[2] We have now shown that **1** reacts with C=O groups to convert them to the C=S moiety. Furthermore, refluxing **1** in methanol gives **3** which may provide some insight into the mechanism of thionation reactions of **1** and **2**.

In a typical reaction **1** (0.3–1 mmol) was refluxed with benzophenone, benzamide or ethyl benzoate (0.6–2 mmol) in toluene–xylene to give the thio analogues in fair yield (55, 86 and 63%, respectively). The purity of the products was established by UV and IR spectroscopy, microanalyses and melting point determination. In general it would appear that **1** is slightly less reactive than **2** with more forcing conditions being required. This difference in the reactivity suggests that it may be possible to use **1** to study the reaction pathways for thionation. Recently there has been a report on the reaction of **2** with alcohols.[3] Reaction of **1** with excess methanol under reflux for 4 hours under N_2 followed by cooling gave very fine colourless needles of **3**. The mass spectrum of **3** has a parent ion at *m*/*z* 362, whilst the IR and Raman spectra reveal the retention of at least one P=S group [ν(PS) 705 cm^{-1}]. The $^{31}P-\{^1H\}$ NMR spectrum consists of two doublets (δ 78.73 and 66.27, J_{P-P} 15 Hz) whilst the ^1H NMR spectrum contains resonances due to the naphtho protons (centred about δ 8.1) and two different methyl groups (δ 3.81 and 2.59, J_{P-H} 16 and 18 Hz, respectively). The spectroscopic data suggested retention of much of the original structure but cannot discriminate between several possible alternatives. Crystals of **3** were grown by diffusion of methanol into a dilute CH_2Cl_2 solution. The X-ray crystal structure† of **3** reveals that reaction has proceeded (Scheme 1) with the opening of the P_2S_2 ring in **1**, elimination of water and formation of the asymmetrically substituted **3** (Fig. 1).‡



Scheme 1 The conversion of **1** to **3** with a possible mechanism

Despite the asymmetry of the substitution on P(1) and P(9) in **3** the $C_{10}P_2S_3$ unit has non-crystallographic C_s symmetry. Furthermore, with respect to this plane, the angles at P(1) and

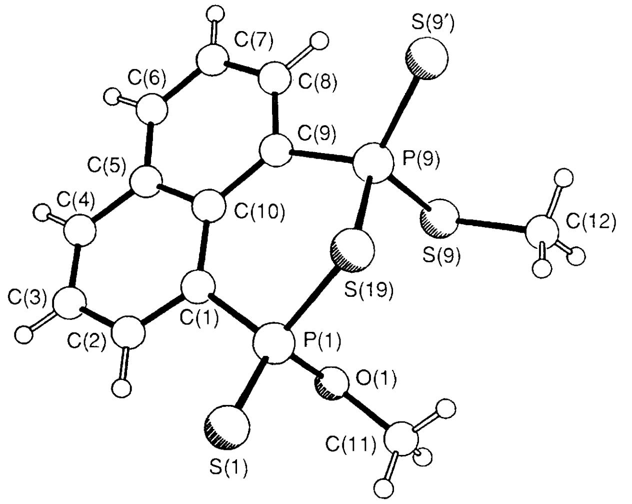


Fig. 1 The X-ray structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.808(3), P(9)–C(9) 1.807(3), P(1)–S(1) 1.923(1), P(1)–O(1) 1.626(3), P(1)–S(19) 2.084(1), P(9)–S(19) 2.079(1), P(9)–S(9′) 1.936(1), P(9)–S(9) 2.079(1); C(1)–C(10)–C(9) 127.8(3), C(10)–C(1)–P(1) 126.6(2), C(10)–C(9)–P(9) 127.1(2), C(1)–P(1)–S(19) 108.2(1), C(9)–P(9)–S(19) 108.2(1), P(1)–S(19)–P(9) 103.0(1), C(1)–P(1)–O(1) 99.9(1), C(1)–P(1)–S(1) 117.7(1), S(1)–P(1)–S(19) 105.6(1), S(1)–P(1)–O(1) 116.8(1), O(1)–P(1)–S(19) 108.1(1), C(9)–P(9)–S(9) 99.2(1), C(9)–P(9)–S(9′) 117.4(1), S(9′)–P(9)–S(19) 105.2(1), S(9′)–P(9)–S(9) 115.4(1), S(9)–P(9)–S(19) 111.5(1).

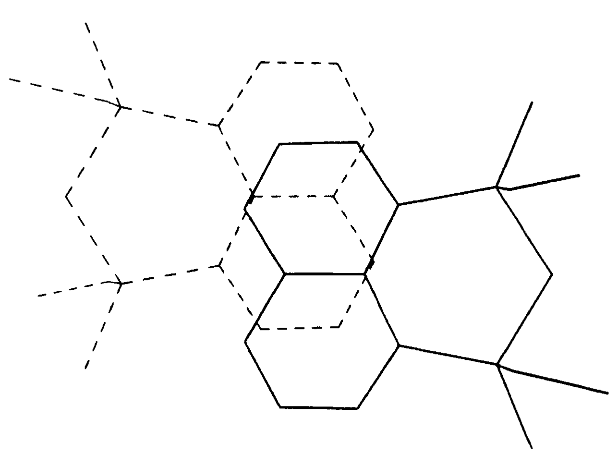


Fig. 2 Line drawing, viewed normal to the plane of the naphthalene rings, showing the stacking of the dimer pairs of **3**

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† *Crystal data* for **3**: $C_{12}H_{12}OP_2S_4$, M = 362.4, monoclinic, a = 6.719(1), b = 21.594(3), c = 10.723(2) Å, β = 102.57(1)°, U = 1519 Å³, space group $P2_1/c$, Z = 4, D_c = 1.59 g cm^{-3}, μ(Cu-Kα) = 76 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by the heavy atom method and refined anisotropically using absorption corrected data to give R = 0.039, R_w = 0.041 for independent observed reflections [$F_0 > 3\sigma(F_0)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Satisfactory C and H microanalyses were obtained.

P(9) are nearly equivalent, the only significant differences being in the O(1)–P(1)–S(19) and the S(9)–P(9)–S(19) angles [108.1(1) and 111.5(1)°, respectively]. The geometry of the C_3P_2S ring differs markedly from that in the parent molecule[1] with the angles at C(1), C(9) and C(10) being significantly enlarged. This is most pronounced at C(1) and C(9) (mean 127 in **3** *vs*. 121° in **1**) although the difference at C(10) is significant [127.8(3) and 124.1(6)° in **3** and **1**, respectively]. The P–C bond lengths are equivalent in both structures [range 1.805(6) –1.809(6) Å]. However, the P–S(19) (bridging sulphur) bond lengths are slightly, but significantly, reduced in **3** *vs*. **1** [2.084(1) and 2.079(1) Å in **3**; *cf*. 2.126(2) and 2.122(1) Å in **1**], there being a concomitant increase in the P(1)–S(1) and P(9)–S(9′) bond lengths [1.923(1) and 1.936(1) Å in **3** *vs*. 1.912(2) and 1.913(1) Å in **1**]. The C_3P_2S ring is significantly flattened compared to that in **1** with S(19) lying only 0.85 Å out of the C_3P_2 plane (*cf*. 1.5 Å in **1**);§ there is also an increase in the P–S–P angle [103.0(1) in **3** *vs*. 80.0(1)° in **1**]. Both the alkoxy and the thioalkoxy groups lie on the same side of the naphthalene ring with the C(1)–P(1)–O(1)–C(11) and C(9)–P(9)–S(9)–C(12) chains adopting *anti* geometries. The molecules pack as overlapping dimer pairs with parallel π-π stacking of the naphthalene rings (Fig. 2) with an interplanar separation of 3.34 Å. The closest non-bonded intermolecular S · · · S distance is 3.57 Å between S(19) and S(9′).

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§ The dihedral angle between the P(1)–C(1)–C(10)–C(9)–P(9) and the P(1)–S(19)–P(19) plane in **3** is 41°.