The Preparation and *X*-Ray Structure of Naphthalenedithiadiphosphetanedisulphide

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Reaction of P_4S_{10} with α-bromonaphthalene at 240 °C gave the title compound, (**1**), in 25% yield, the first example of a six-membered (C_3P_2S) organo-P–S ring, the *X*-ray structure of which reveals a novel folded P_2S_2 ring.

There is currently interest in the preparation of organic sulphur-nitrogen heterocycles.[1] However there are very few examples of organophosphorus–sulphur ring compounds. Phosphorus sulphides such as P_4S_{10} and $RP(S)S_2P(S)R$ (R = $MeOC_6H_5$– = Lawessons Reagent) are important in organic synthesis as thionating agents.[2] Apart from being of interest in their own right, new carbon containing phosphorus–sulphur heterocycles may offer the opportunity of variable selectivity in synthesis. Here we report the preparation of the first example of a six-membered organothiophosphate heterocycle. To our knowledge there are no known examples of this ring system although there has been a brief report on the preparation of $C_6H_4(PMe_3)_2S$ which is believed to have a structure containing a C_2P_2S ring.[3]

Reaction of P_4S_3 with S_8 in α-bromonaphthalene at 240 °C is reported[4] to give P_4S_9 in moderate yield. However the reaction is very sensitive to the conditions used. We have found that in order to maximise the yield of P_4S_9 a slightly lower temperature (*ca.* 220 °C) is preferable. If the temperature is raised to 240 °C, and above, compound (**1**) is obtained after cooling and addition of diethyl ether. Alternatively, (**1**) may be prepared in 25% yield by reaction of P_4S_{10} with bromonaphthalene. Reaction of P_4S_{10} with naphthalene also gives (**1**) but in lower yield together with at least five other compounds which we have not yet identified.

The *X*-ray structure of (**1**) (Figure 1)† shows the naphtho$(PS)_2$ unit to be planar (all of the atoms lying within a crystallographic mirror plane) and symmetrically bridged by two sulphur atoms. The molecule has, within statistical significance, C_{2v} symmetry. The geometry of the naphthalene ring and the C–P and P=S distances are as expected. However, the geometry of the P_2S_2 ring is noteworthy. The ring is non-planar with a dihedral angle of 135° about the S · · · S′ axis. The two S–P–S angles [91.6(1), 91.8(2)°] and the P–S–P angles [80.0(1)°] are noticeably reduced relative to those in $RP(S)S_2P(S)R$ systems [R = Me,[5] Ph,[6] 2,4,6-$Me_3C_6H_2$[7] S–P–S 94.5(2), 93.1(1), and 93.8(1), P–S–P 85.5(2), 86.9(1), and 86.2(1)°, respectively]. The transannular S(19) · · · S(19)′ distance is 3.05 Å.‡ The molecules pack parallel to each other (interplanar separation between naphtho rings 3.56 Å) though with a minimum of overlap between adjacent naphtho rings.§

In view of the usefulness of Lawessons Reagent in organic synthesis we have investigated the ability of (**1**) to behave as a thionating agent. Both triphenylphosphine oxide and benzophenone are readily converted to the corresponding sulphide. Reaction of (**1**) with triphenylphosphine proceeds at room temperature to give $SPPh_3$ and an as yet unidentified ring system.

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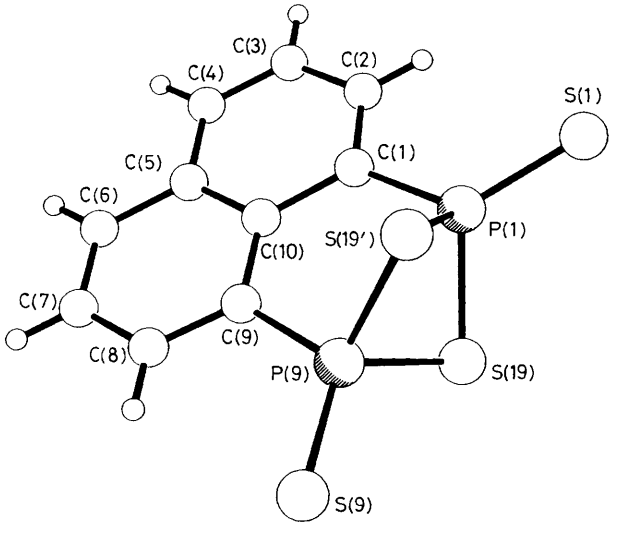

Figure 1. The *X*-ray crystal structure of (**1**). Important bond distances and angles: C(1)–P(1) 1.805(6), C(9)–P(9) 1.809(6), P(1)–S(1) 1.913(2), P(9)–S(9) 1.912(2), P(1)–S(19) 2.126(2), P(9)–S(19) 2.122(1), S(19) · · · S(19′) 3.05 Å; C(1)–P(1)–S(1) 117.5(2), C(9)–P(9)–S(9) 116.9(2), C(1)–P(1)–S(19) 103.7(1), C(9)–P(9)–S(19) 103.6(1), S(1)–P(1)–S(19) 118.2(1), S(9)–P(9)–S(19) 118.6(1), S(19)–P(1)–S(19′) 91.6(1), S(19)–P(9)–P(19′) 91.8(1), P(1)–S(19)–P(9) 80.0(1)°.

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† *Crystal data* for (**1**): $C_{10}H_6P_2S_4$, M = 316.4, orthorhombic, a = 7.116(1), b = 9.209(1), c = 9.494(3) Å, U = 1244 Å^3, space group *Pmcn*, Z = 4, D_c = 1.69 gcm^{-3}, μ(Cu-K_α) = 92 cm^{-1}. Data were collected on a Nicolet R3m diffractometer using graphite-monochromated Cu-K_α radiation, ω-scans. The structure was solved by direct methods, corrected for absorption, and refined anisotropically to give R = 0.048, R_w = 0.051 for 834 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, θ ≤58°]. 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.

‡ The shortest intermolecular S · · · S contacts are between S(9) and S(19), 3.38 Å, and S(1) and S(9), 3.48 Å.

§ In adjacent molecules H(2′) lies approximately over the centre of the C(5)—C(10) ring.