NOTIZEN

Preparation and Crystal Structure of the Hydrogen-Bonded Cyclic Dimer of $PhP(S)[N(CH_2Ph)_2]OH$, $HN(CH_2Ph)_2$ ‡

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The structure of the title compound was determined by X-ray crystallography. The compound is a cyclic dimer with short N···O and N···S contacts.

Phenylphosphonothioic dichloride, $PhP(S)Cl_2$, reacts with dibenzylamine in benzene at room temperature to give five crystalline products containing phosphorus[1]. One of these products has the empirical formula, $C_{34}H_{35}N_2OPS$ (1). Compound **1** is only formed in the presence of water. NMR data indicate compound **1** contains a dibenzylamino group directly bonded to phosphorus and one other molecule of dibenzylamine. It was originally suggested[1] that compound **1** was probable a salt-like material, $[NH_2(CH_2Ph)_2]^+\{PhP(S)[N(CH_2Ph)_2]O\}^-$. An X-ray investigation was undertaken to clarify the bonding.

Experimental

A solution of dibenzylamine (78.8 g, 0.4 mole) in benzene (200 ml) was shaken with distilled water (50 ml) and then added dropwise to a stirred solution of phenyldichlorophosphine sulphide (21.2 g, 0.10 mole) in benzene (400 ml). The mixture was allowed to stand for 36 h. Dibenzylamine hydrochloride was filtered off and the solvent evaporated to dryness. The oily residue obtained was dissolved in diethyl ether and the remaining traces of dibenzylamine hydrochloride were filtered off. A product gradually precipitated from the filtrate which was recrystallised from diethyl ether and light petroleum b.p. 60–80 °C (1:1) to give colourless crystals of compound **1** m.p. 124 °C, (17 g, 31%).

$C_{34}H_{35}N_2OPS$

Calcd	C 74.2	H 6.4	N 5.1	P 5.7	S 5.8,
Found	C 74.1	H 6.4	N 5.1	P 5.6	S 5.8.

The crystals are monoclinic with $a = 18.22 \pm 0.01$, $b = 10.21 \pm 0.01$, $c = 16.63 \pm 0.01$ Å, $\beta = 97.8 \pm 0.1°$; $\gamma = 3065$ Å^3, space group $P2_1/n$, $D_{calc} = 1.203$ g/cm^3 for $Z = 4$, $D_{exp} = 1.236$, MW = 550; 1269 independent reflections significantly above the background using CuKα radiation: $R = 0.10$.

The unit cell is constructed from dimers of **1** which are formed with hydrogen-bonds about a centre of symmetry. Within the complex the P–O and P–S interatomic distances are 1.56 ± 0.01 and 1.997 ± 0.007 Å respectively which can be compared with 1.46 ± 0.01 Å for P–O in triphenylphosphine oxide[2] and 1.64 ± 0.01 Å in the hydroxytriphenylphosphonium ion[3] (Ph_3POH^+), and 1.936 ± 0.005 Å for P–S in tri-*meta*-tolylphosphine sulphide[4]. A

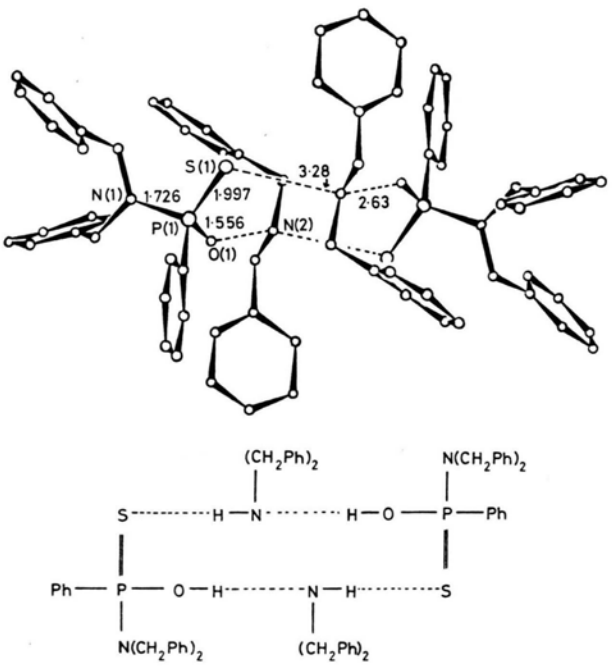

Figure. Selected interatomic distances for $PhP(S)[N(CH_2Ph)_2]OH$, $HN(CH_2Ph)_2$.

‡ *Dedicated to Professor Dr.* Leopold Horner *on his 65th birthday.*

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difference Fourier synthesis calculated at the end of the refinement indicated reasonable positions for the two hydrogen atoms of the hydrogen bonds. One is 0.99 Å from the dibenzylamine nitrogen and 2.31 Å from the sulphur atom, the other is 1.45 Å from the nitrogen and 1.30 Å from the oxygen atom (Figure).

Thus, the main form of the complex is $PhP(S)[N(CH_2Ph)_2]OH,HN(CH_2Ph)_2$ although there may be some contribution from

$\{PhP(S)[N(CH_2Ph)_2]O\}^-[H_2N(CH_2Ph)_2]^+$.

The O···N(2) and N(2)···S interatomic separations are 2.61 ± 0.01 and 3.28 ± 0.01 Å respectively. The O···N distance is slightly shorter than the expected values[5] (2.7–3.2 Å) for a hydrogen-bond, and the N···S distance is also shorter than that (3.44 Å) observed[6] for the corresponding bond in ethylene thiourea. Both bonds therefore are among the strongest reported hydrogen-bonds of their type and they are probably responsible for the curious difference in reactivity of the complex once it has crystallised from solution[1].

The P–N(1) bond length of 1.73 ± 0.01 Å is closer to the single bond length[7] of 1.79 Å than to that of 1.57 Å in cyclophosphazenes where there is considerable π-delocalisation[8]. Presumably the remaining electron of phosphorus is associated almost entirely in π-bonding to the sulphur and oxygen atoms.

The dimensions of the rest of the molecule are as expected.

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[1] J. D. Healy, R. A. Shaw, B. C. Smith, C. P. Thakur, and M. Woods, J. Chem. Soc. Dalton **1974**, 1286.

[2] G. Bandoli, G. Bartolozzo, D. A. Clemente, U. Croatto, and C. Panattoni, J. Chem. Soc. (A) **1970**, 2778.

[3] T. S. Cameron and C. K. Prout, J. Chem. Soc. (C) **1969**, 2289.

[4] T. S. Cameron, K. D. Howlett, R. A. Shaw, and M. Woods, Phosphorus **3**, 71 [1973].

[5] International Tables for X-ray Crystallography, Vol. **III**, Kynoch Press, Birmingham 1969.

[6] P. J. Wheatley, Acta Crystallogr. **6**, 369 [1953].

[7] T. S. Cameron and Kh. Mannan, Acta Crystallogr., in the press.

[8] D. E. C. Corbridge, The Structural Chemistry of Phosphorus, p. 337, Elsevier, Netherlands 1974.