

Reduction of Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents. Part XIV.¹ X-Ray Crystallographic Determination of the Structures of 3-(2,6-Dimethylphenyl)-2,3-dihydro-2,2,2-trimethoxy-1,3,2-benzoxazaphosph(v)ole and its 2-Hydroxy-2-oxo-analogue

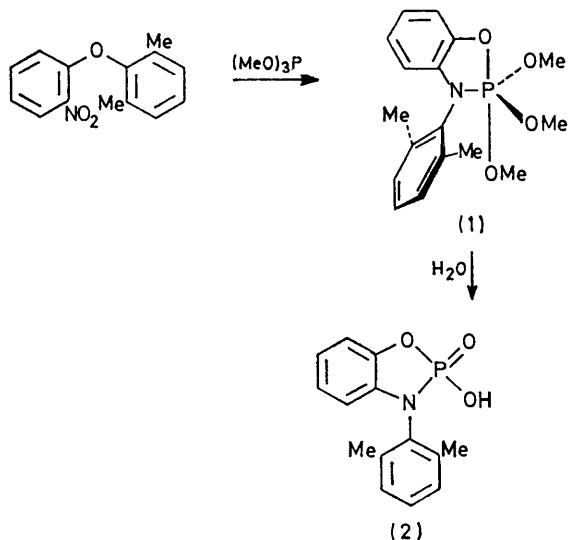
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3-(2,6-Dimethylphenyl)-2,3-dihydro-2,2,2-trimethoxy-1,3,2-benzoxazaphosph(v)ole (1) is a trigonal bipyramidal phosphorus compound with only slight deviation from ideal geometry. The five-membered oxazaphosphole ring is planar and occupies an apical-equatorial site with apical oxygen and equatorial nitrogen, the latter being sp^3 -hybridised. The pendant *N*-(2,6-dimethylphenyl) ring is almost completely orthogonal to the second benzene ring. The crystals are monoclinic with $a = 6.93(2)$, $b = 20.26(4)$, $c = 12.13(8)$ Å, $\beta = 96.7(4)^\circ$, space group $P2_1/n$.

The 2-hydroxy-2-oxo-analogue (2) also exhibits orthogonality of the *N*-(2,6-dimethylphenyl) ring. The oxazaphosphole ring is almost planar and exhibits distorted tetrahedral geometry about phosphorus (O-P-N angle 96.3°). The crystals are monoclinic with $a = 10.786(5)$, $b = 13.222(5)$, $c = 9.634(4)$ Å, $\beta = 90.0(1)^\circ$, space group $P2_1/c$.

THE two preceding papers^{1,2} describe the conversion of a series of aryl 2-nitroaryl ethers into 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles by reaction with tervalent phosphorus reagents. In particular 2,6-dimethylphenyl 2-nitrophenyl ether on reaction with trimethyl phosphite gave 3-(2,6-dimethylphenyl)-2,3-dihydro-2,2,2-trimethoxy-1,3,2-benzoxazaphosph(v)ole (1), which was converted into the 2-hydroxy-2-oxo-analogue (2) in moist air. To the former phosphole was assigned a trigonal

graphic analysis were obtained by recrystallisation from light petroleum (b.p. 60–80°) and benzene, respectively. Crystals of (2) were colourless needles, elongated along [011], and were stable in air. A single specimen was used to collect data for the three principal zones and ten layers normal to [011] by Weissenberg photography (Cu- $K\alpha$ radiation). Cell dimensions were refined by using the $\alpha_1 - \alpha_3$ splitting of twenty high angle, zero-level reflections. Crystals of (1), also colourless needles, were hydrolysed rapidly in moist air. An irregular specimen was mounted in a glass capillary tube under nitrogen, and ten layers were collected normal to [201]. Cell dimensions were obtained from these photographs, and from a zero-layer photograph of another specimen, mounted parallel to [010]. Crystal data for the two compounds are given in Table 1. The non-



bipyramidal structure (1) in which the P-N bond is equatorial and the *N*-(2,6-dimethylphenyl) group is orthogonal to the second benzene ring, on the basis of analytical, ^1H and ^{31}P n.m.r., and chemical evidence. The structure of the tetraco-ordinate phosphole (2) was deduced similarly. We now report the results of an X-ray crystallographic study which fully confirms these conclusions.

EXPERIMENTAL

The oxazaphospholes (1) and (2) were prepared as described earlier.² Suitable crystals for X-ray crystallo-

¹ Part XIII, J. I. G. Cadogan, D. S. B. Grace, and B. S. Tait, preceding paper.

Compound	(1)	(2)
Molecular formula	$\text{C}_{17}\text{H}_{22}\text{NO}_4\text{P}$	$\text{C}_{14}\text{H}_{14}\text{NO}_3\text{P}$
<i>M</i>	335	275
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Cell constants: <i>a</i>	6.93(2) Å	10.786(5) Å
<i>b</i>	20.26(4)	13.222(5)
<i>c</i>	12.13(8)	9.634(4)
β	96.7(4)°	90.0(1)°
<i>U</i>	1 690 Å ³	1 372 Å ³
D_o	1.317 g cm ⁻³	1.333 g cm ⁻³
D_m		1.327
<i>Z</i>	4	4
<i>F</i> (000)	712	576
Independent observations	948	1 863

standard setting of the space group of (1) was chosen to give a nearly orthogonal cell.

For (2), 1 863 independent intensities were measured visually, by using a calibrated intensity strip, and were put onto a common scale by common reflections. No absorption corrections were applied, but an empirical correction for secondary extinction was applied to the 15 strongest intensities in the final stages of refinement. Irregular absorption by the capillary made accurate estimation of intensities difficult for (1) but a final set of 939 independent intensities was obtained as above. Interlayer scale factors were refined from initial values based on exposure times.

For both compounds, the position of the phosphorus atom was obtained readily from a sharpened Patterson function,

² J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J.C.S. Perkin I*, 1975, 2376.

and all the other non-hydrogen atoms were located in a Fourier synthesis phased by the phosphorus atom. Significant peaks were found near estimated hydrogen positions

TABLE 2

Fractional co-ordinates for (2) *							
Atom	10 ⁴ x	10 ⁴ y	10 ⁴ z	Atom	10 ⁴ x	10 ⁴ y	10 ⁴ z
P	1 109(1)	4 657(1)	3 295(1)	H(2)	46(9)	481(7)	625(10)
O(1)	1 206(4)	3 538(3)	2 675(4)	H(3)	384(6)	525(6)	-1(7)
O(2)	-204(4)	5 053(4)	3 608(4)	H(4)	423(6)	375(5)	-132(7)
O(3)	1 482(4)	4 689(3)	4 768(4)	H(5)	353(7)	221(6)	-72(8)
N	2 069(4)	5 187(3)	2 184(4)	H(6)	199(5)	209(5)	113(6)
C(1)	2 038(5)	3 517(4)	1 555(6)	H(9)	451(7)	768(6)	342(8)
C(2)	2 533(4)	4 447(4)	1 266(5)	H(10)	345(7)	888(7)	221(7)
C(3)	3 369(5)	4 481(5)	190(18)	H(11)	157(9)	838(7)	84(10)
C(4)	3 684(7)	3 709(6)	-566(7)	H(131)	455(6)	524(6)	326(7)
C(5)	3 192(6)	2 787(5)	-271(7)	H(132)	366(6)	555(6)	463(6)
C(6)	2 349(6)	2 668(5)	811(6)	H(133)	487(11)	613(10)	398(12)
C(7)	2 449(4)	6 219(12)	2 172(5)	H(141)	102(21)	604(6)	-11(7)
C(8)	3 466(5)	6 506(5)	2 982(6)	H(142)	39(11)	736(10)	-1(13)
C(9)	3 810(7)	7 513(5)	2 996(7)	H(143)	-10(14)	618(11)	92(14)
C(10)	3 163(8)	8 210(5)	2 230(7)				
C(11)	2 915(7)	7 912(5)	1 399(7)				
C(12)	1 803(5)	6 916(4)	1 349(6)				
C(13)	4 185(6)	5 746(6)	3 799(7)				
C(14)	736(7)	6 591(7)	444(10)				

* Hydrogen atoms are shown adjacent to the atoms to which they are bonded.

in (2), but the difference Fourier for (1) was not sufficiently clear to enable hydrogen positions to be determined. Both structures were refined isotropically by using full matrix least squares and unit weights. In the final cycles of refinement, a weighting scheme was introduced to minimise $\sum w(|F_o| - |F_c|)^2$ with $w = (|F_o|/16)^2$ for $F_o < 16$, and $w = (16/|F_o|)^2$ otherwise. For (1), anisotropic thermal parameters were used for the phosphorus atom only; in (2) anisotropic thermal parameters were given to all non-hydrogen atoms, and hydrogen atoms were refined isotropically. For storage reasons, a block diagonal approximation was used for (2). At convergence (no shift of a positional parameter greater than 0.3 of its standard deviation) R was 0.135 for (1) and 0.088 for (2). Positional and

Tables 5 and 6. For all standard crystallographic computing the programs of the 'X-Ray '70' system³ were used, as implemented at the Edinburgh Regional Computing Centre.

DISCUSSION

3-(2,6-Dimethylphenyl)-2,3-dihydro-2,2,2-trimethoxy-1,3,2-benzoxazaphosph(v)ole (1) (Figure 1).—The com-

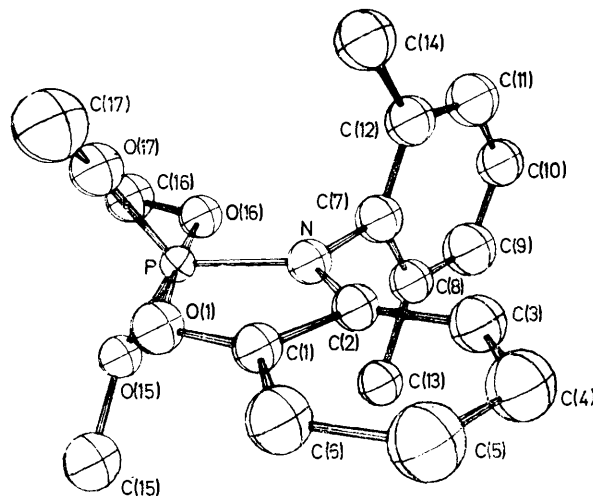


FIGURE 1 The 2,2,2-trimethoxybenzoxazaphosphole (1)

pound shows trigonal bipyramidal geometry about phosphorus with only slight deviations from the ideal bond angles (Table 6). The five-membered oxazaphosphole ring occupies an apical-equatorial site with apical oxygen [O(1)] and equatorial nitrogen in accord with the relative apicophilicities of the phenoxy- and amino-ligands.⁴

TABLE 3
Thermal parameters for (2) *

Atom	10 ⁵ U ₁₁	10 ⁵ U ₂₂	10 ⁵ U ₃₃	10 ⁵ U ₁₂	10 ⁵ U ₁₃	10 ⁵ U ₂₃	Atom	10 ³ U
P	4 915(3)	4 722(3)	4 136(3)	-12(2)	938(2)	227(2)	H(2)	88(31)
O(1)	7 162(11)	4 749(8)	4 874(10)	-738(8)	1 307(8)	20(7)	H(3)	46(18)
O(2)	4 521(9)	7 807(10)	5 152(10)	862(7)	1 112(8)	649(8)	H(4)	44(17)
O(3)	6 076(10)	6 437(9)	3 722(9)	740(8)	1 030(7)	511(7)	H(5)	73(23)
N	4 330(9)	3 881(9)	4 003(10)	-167(7)	1 115(8)	-235(7)	H(6)	29(15)
C(1)	4 746(12)	5 242(12)	4 481(13)	0(10)	-597(10)	-879(9)	H(9)	60(20)
C(2)	3 281(10)	4 921(11)	4 160(12)	237(8)	-183(9)	-769(9)	H(10)	58(19)
C(3)	5 101(13)	6 761(14)	4 908(14)	-126(11)	940(11)	-417(11)	H(11)	86(28)
C(4)	7 330(18)	9 868(19)	5 386(16)	972(15)	1 551(14)	-2 937(14)	H(131)	33(17)
C(5)	5 915(14)	8 028(16)	5 860(16)	1 891(12)	-922(13)	-3 291(13)	H(132)	30(11)
C(6)	6 062(14)	5 810(14)	5 527(15)	705(11)	-911(12)	-1 430(11)	H(133)	107(39)
C(7)	3 552(10)	4 291(10)	3 377(10)	129(8)	868(8)	139(8)	H(141)	44(19)
C(8)	5 114(13)	4 461(12)	4 223(13)	-139(10)	360(10)	-238(9)	H(142)	124(44)
C(9)	7 868(18)	6 218(14)	5 704(17)	-1 608(13)	851(14)	-609(12)	H(143)	144(48)
C(10)	9 983(22)	4 258(13)	7 473(21)	-842(13)	2 033(17)	-609(12)		
C(11)	7 829(18)	5 701(14)	6 384(14)	1 541(13)	1 235(15)	1 582(12)		
C(12)	4 878(12)	5 052(12)	4 841(14)	582(10)	557(11)	740(9)		
C(13)	5 439(15)	9 030(18)	5 857(17)	796(13)	-648(13)	1 061(13)		
C(14)	6 590(17)	9 858(20)	6 213(19)	1 005(15)	-1 664(15)	1 578(15)		

* Temperature factors are of the form: $\exp(-2\pi^2 \sum_i \sum_j a_i a_j h_i h_j U_{ij})$ or $\exp(-\pi^2 U \sin^2 \theta / \lambda^2)$.

thermal parameters for (2) are given in Tables 2 and 3, and for (1) in Table 4. The structure factor tables are deposited as Supplementary Publication No. SUP 21511 (6 pp.).† Bond lengths and angles are given for both compounds in

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

There are two equatorial *P*-methoxy-groups including O(15) and O(17) and one axial *P*-methoxy-group

³ 'X-Ray '70,' Technical Report TR-192 of the Computer Science Centre, University of Maryland, July 1970.

⁴ P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsohis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

TABLE 4

Fractional co-ordinates and thermal parameters for (1)

Atom	10 ⁴ x	10 ⁴ y	10 ⁴ z	10 ⁴ U
P	3 382(7)	6 414(2)	6 686(4)	*
N	2 504(21)	5 859(6)	7 527(12)	327(33)
O(1)	2 728(18)	7 017(5)	7 604(10)	372(29)
O(15)	2 100(16)	6 758(4)	5 652(8)	327(27)
O(16)	3 927(18)	5 820(4)	5 894(10)	374(28)
O(17)	5 527(17)	6 675(5)	6 829(9)	441(31)
C(1)	1 947(26)	6 807(6)	8 466(13)	292(39)
C(2)	1 725(26)	6 107(6)	8 456(14)	300(38)
C(3)	813(29)	5 772(7)	9 279(15)	416(43)
C(4)	167(32)	6 142(8)	10 097(17)	525(51)
C(5)	360(30)	6 835(8)	10 134(16)	538(50)
C(6)	1 237(28)	7 170(7)	9 281(14)	427(45)
C(7)	2 583(28)	5 141(8)	7 411(16)	440(406)
C(8)	974(26)	4 838(7)	6 833(14)	414(44)
C(9)	909(33)	4 153(9)	6 766(17)	670(58)
C(10)	2 420(29)	3 798(8)	7 330(16)	506(52)
C(11)	3 976(31)	4 095(8)	7 838(16)	592(54)
C(12)	4 122(28)	4 790(7)	7 947(15)	474(47)
C(13)	- 712(27)	5 235(7)	6 315(14)	426(46)
C(14)	5 848(30)	5 164(9)	8 536(16)	615(57)
C(15)	636(30)	7 248(8)	5 651(15)	547(51)
C(16)	4 831(32)	5 931(8)	4 906(18)	529(52)
C(17)	6 382(32)	7 104(9)	7 772(18)	690(58)

10 ⁴ U ₁₁	10 ⁴ U ₂₂	10 ⁴ U ₃₃	10 ⁴ U ₁₂	10 ⁴ U ₁₃	10 ⁴ U ₂₃
* 242(33)	268(16)	310(28)	- 5(22)	5(29)	56(21)

including O(16). The endocyclic apical bond P-O(1) is longer than the endocyclic equatorial bond P-N and the exocyclic apical bond P-O(16) is longer than the exocyclic equatorial bond P-O(17) but only just longer than the other equatorial bond P-O(15). The oxazaphosphole bonds O(1)-C(1) and N-C(2) are comparatively short (Table 5). The benzazaphosphole ring is

TABLE 5

Bond distances (Å) in (1) and (2)

Bond	Length in (2)	Length in (1)	Bond	Length in (2)
P-N	1.646(4)	1.68(1)	C(3)-H(3)	1.04(8)
P-O(1)	1.599(4)	1.75(1)	C(4)-H(4)	0.94(7)
P-O(2)	1.526(5)		C(5)-H(5)	0.95(8)
P-O(3)	1.476(4)		C(6)-H(6)	0.91(6)
P-O(15)		1.60(1)	C(9)-H(9)	0.89(7)
P-O(16)		1.61(1)	C(10)-H(10)	0.94(8)
P-O(17)		1.57(1)	C(11)-H(11)	1.06(9)
O(1)-C(1)	1.404(7)	1.30(2)	C(13)-H(131)	0.93(7)
C(1)-C(2)	1.369(7)	1.43(2)	C(13)-H(132)	1.02(6)
C(2)-C(3)	1.385(8)	1.42(3)	C(13)-H(133)	0.91(12)
C(3)-C(4)	1.405(10)	1.36(3)	C(14)-H(141)	0.95(10)
C(4)-C(5)	1.360(10)	1.41(2)	C(14)-H(142)	1.17(13)
C(5)-C(6)	1.392(9)	1.43(3)	C(14)-H(143)	1.15(15)
C(6)-C(1)	1.373(8)	1.37(2)	O(2)-H(2)	0.74(10)
C(2)-N	1.411(6)	1.40(2)	O(3)*-H(2)	1.81(10)
C(7)-N	1.425(16)	1.46(2)		
C(7)-C(8)	1.399(8)	1.39(2)		
C(7)-C(12)	1.400(7)	1.38(3)		
C(8)-C(9)	1.382(9)	1.39(2)		
C(9)-C(10)	1.371(10)	1.38(3)		
C(10)-C(11)	1.373(11)	1.32(3)		
C(11)-C(12)	1.384(9)	1.42(2)		
C(8)-C(13)	1.494(9)	1.51(2)		
C(12)-C(14)	1.507(11)	1.52(3)		
O(15)-C(15)		1.42(2)		
O(16)-C(16)		1.43(3)		
O(17)-C(17)		1.50(2)		

* At -x, 1 - y, 1 - z.

This planarity aids the back donation of electrons from the nitrogen lone pair orbital to phosphorus. In this example, back donation will be particularly favourable as the five-membered ring is in the apical plane, causing

TABLE 6
Bond angles (°) in (1) and (2)

Angle	In (2)	In (1)	Angle	In (2)	In (1)	Angle	In (2)
O(1)-P-O(2)	108.9(2)		C(2)-C(3)-C(4)	116.1(6)	117.5(14)	C(2)-C(3)-H(3)	125(4)
O(1)-P-O(3)	111.5(2)		C(3)-C(4)-C(5)	122.2(7)	122.3(18)	C(4)-C(3)-H(3)	119(4)
O(2)-P-N	110.3(3)		C(4)-C(5)-C(6)	120.9(6)	119.7(17)	C(3)-C(4)-H(4)	121(4)
O(3)-P-N	116.1(3)		C(1)-C(6)-C(5)	117.2(6)	119.0(14)	C(5)-C(4)-H(4)	117(4)
O(2)-P-O(3)	112.4(2)		N-C(7)-C(8)	118.8(9)	116.9(15)	C(4)-C(5)-H(5)	118(5)
O(1)-P-N	96.3(2)	86.7(7)	N-C(7)-C(12)	119.4(6)	120.2(15)	C(6)-C(5)-H(5)	120(5)
O(1)-P-O(15)		91.9(6)	C(8)-C(7)-C(12)	121.8(12)	122.7(15)	C(1)-C(6)-H(6)	114(4)
O(1)-P-O(16)		176.0(6)	C(7)-C(8)-C(13)	121.3(8)	119.8(13)	C(5)-C(6)-H(6)	128(4)
O(1)-P-O(17)		90.4(6)	C(7)-C(8)-C(9)	118.5(8)	119.3(16)	C(8)-C(9)-H(9)	118(5)
O(15)-P-O(16)		90.3(7)	C(9)-C(8)-C(13)	120.2(6)	120.8(15)	C(10)-C(9)-H(9)	121(5)
O(15)-P-O(17)		111.8(6)	C(8)-C(9)-C(10)	120.3(6)	118.2(17)	C(9)-C(10)-H(10)	119(5)
O(15)-P-N		123.9(7)	C(9)-C(10)-C(11)	120.6(6)	121.4(16)	C(11)-C(10)-H(10)	120(5)
O(16)-P-O(17)		91.8(6)	C(10)-C(11)-C(12)	121.7(6)	122.8(17)	C(10)-C(11)-H(11)	128(5)
O(16)-P-N		89.3(7)	C(7)-C(12)-C(14)	121.4(8)	119.1(14)	C(12)-C(11)-H(11)	110(5)
O(17)-P-N		124.3(7)	C(11)-C(12)-C(14)	121.7(6)	125.6(16)	C(8)-C(13)-H(131)	115(4)
P-O(1)-C(1)	110.3(4)	116.5(9)	C(7)-C(12)-C(11)	117.0(7)	115.2(16)	C(8)-C(13)-H(132)	107(4)
P-N-C(2)	109.6(4)	116.7(10)				C(8)-C(13)-H(133)	99(8)
P-N-C(7)	126.5(4)	126.0(13)				H(131)-C(13)-H(132)	119(5)
P-O(15)-C(15)		129.3(10)				H(131)-C(13)-H(133)	99(9)
P-O(16)-C(16)		122.4(9)				H(132)-C(13)-H(133)	116(8)
P-O(17)-C(17)		124.3(12)				C(12)-C(14)-H(141)	107(12)
C(2)-N-C(7)	123.9(4)	117.2(13)				C(12)-C(14)-H(142)	102(6)
O(1)-C(1)-C(2)	112.9(5)	111.8(14)				C(12)-C(14)-H(143)	120(7)
O(1)-C(1)-C(6)	124.9(5)	128.4(13)				H(141)-C(14)-H(142)	124(8)
C(2)-C(1)-C(6)	122.2(5)	119.6(15)				H(141)-C(14)-H(143)	97(12)
N-C(2)-C(3)	127.7(5)	129.9(13)				H(142)-C(14)-H(143)	108(9)
N-C(2)-C(1)	110.9(5)	108.3(14)				P-O(2)-H(2)	108(8)
C(1)-C(2)-C(3)	121.4(5)	121.8(15)				O(2)-H(2)-O(3)*	164(16)

* At -x, 1 - y, 1 - z.

nearly planar, as is the 2,6-dimethylphenyl group, and these two planes are nearly orthogonal, requiring the nitrogen atom to be *sp*²-hybridised; in accord with this the sum of the bond angles around nitrogen is 360°.

the nitrogen *p*_z lone-pair orbital to lie in the equatorial plane, an orientation which has been predicted⁵ to be

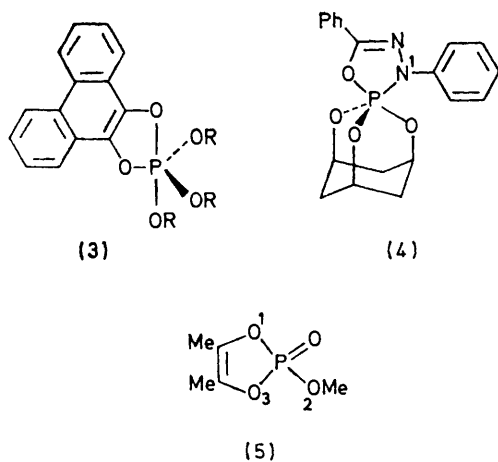
⁵ R. Hoffmann, J. M. Howell, and E. C. Muettterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

ideal for maximum pd overlap. Indeed, the P-N bond length is only 1.68 Å, whereas a single P-N bond should be *ca.* 1.8 Å.⁶

That the apical bonds to phosphorus are longer than the equatorial bonds is in accord with greater back donation from equatorial ligands to the empty d orbitals of phosphorus.⁷ That the P-O(1) bond is very long and the O(1)-C(1) and N-C(2) bonds are short, lends weight to the view^{8,9} that competition occurs for the electron density on the phosphorus ligands, the oxygen and nitrogen atoms in this case, between the empty d orbitals of phosphorus and the π -electron cloud of adjacent aromatic systems. In the case of the 2,6-dimethylphenyl ring the observed orthogonality much reduces the possibility of delocalisation involving the nitrogen lone pair.

The related structures (3; R = alkyl) and (4) show similar features.^{8,9} Thus in (4), the phenyl substituent on the sp^2 -hybridised nitrogen [N(1)] is almost orthogonal to the plane of the oxadiazaphosphole ring. This suggests that the steric effect of the *ortho*-methyl groups of the oxazaphosphole (Figure 1) which prevents rotation about the bond N-C(7) is not the only reason for the near orthogonality of the 2,6-dimethylphenyl group to the plane of the oxazaphosphole ring, and that compounds in the series without blocking *ortho*-groups should show the same features. In accord with this, ¹H n.m.r. studies¹ predict orthogonality in *N*-phenyl analogues of (1).

The most significant deviation from trigonal bipyramidal geometry in (1) lies in the much compressed (-8°) diequatorial exocyclic O(15)-P-O(17) angle, the



C(7)-N-P angle being correspondingly expanded. The exocyclic apical equatorial O-P-O angles are all close to 90° , indicating much less steric interaction with the apical methoxy-ligands, as is to be expected.

3-(2,6-Dimethylphenyl)-2,3-dihydro-2-hydroxy-2-oxo-

⁶ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1962, p. 105.

⁷ F. Ramirez and I. Ugi, *Adv. Phys. Org. Chem.*, 1971, **9**, 26.

⁸ W. C. Hamilton, R. D. Spratley, and J. Ladell, *J. Amer. Chem. Soc.*, 1967, **89**, 2272.

1,3,2-benzoxazaphosph(v)ole (2) (Figure 2).—Compound (2) has an almost planar five-membered oxazaphosphole ring with distorted tetrahedral geometry about the phosphorus atom with angles ranging from 96.3

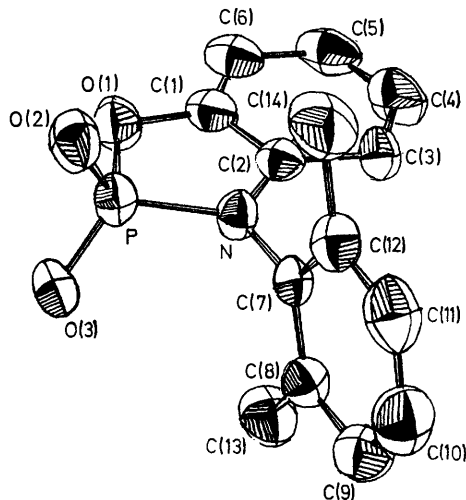


FIGURE 2 The 2-hydroxy-2-oxobenzoxazaphosphole (2)

to 112.4° (Table 6) (*cf* the tetrahedral angle, 109.5°). The nitrogen atom is sp^2 -hybridised and overlap of the filled p orbital with either an empty d orbital of phosphorus or the electron-cloud at C(2) of the benzene ring is possible. Again the planes of the oxazaphosphole ring and the 2,6-dimethylphenyl group are nearly orthogonal.

Ramirez and his co-workers¹⁰ determined the crystal structure of the dioxaphosphole (5), which had an essentially planar ring and distorted tetrahedral geometry about the phosphorus atom. Both this and the oxazaphosphole (2) show angle strain at phosphorus as revealed by the small angles O(1)-P-N (96.3°) in (2) and O(1)-P-O(3) (98.5°) in compound (5).

There also seems to be evidence for competition between the d orbitals of phosphorus and the π -electron cloud on the adjacent unsaturated systems for the filled p orbitals of O(1) and N in (2), and O(1) and O(3) in compound (5). Thus in (2) the endocyclic bonds P-O(1) and P-N are appreciably longer than the exocyclic single bond P-O(2) and in compound (5) the endocyclic bonds P-O(1) and P-O(3) are appreciably longer than the exocyclic single bond P-O(2). Similarly the endocyclic bonds O(1)-C(1) and N-C(2) in (2), and C(1)-O(1) and C(2)-O(3) in (5) are short in comparison with the exocyclic bond C(5)-O(2) in (5).

The analysis revealed a dimeric structure in the crystal, the two halves of the dimer being related by a crystallographic centre of symmetry arising from hydrogen bonding between the P(O)OH groups of adjacent molecules (Tables 5 and 6).

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⁹ F. Ramirez, L. Kramer, P. Stern, J. Ricci, and W. Hamilton, *J. Amer. Chem. Soc.*, 1973, **95**, 6335.

¹⁰ F. Ramirez, O. Modan, C. Smith, D. Swank, and C. Caughlan, *J. Amer. Chem. Soc.*, 1967, **89**, 6503.