

2,3,8,8-Tetraphenyl-[1,3,2λ⁵]oxazaphospholino[2,3-*b*]benzo[*d*][1,3,2λ⁵]oxazaphospholine

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Abstract. C₃₂H₂₄NO₂P, monoclinic, *C*2/*c*, *a* = 24.556 (5), *b* = 8.816 (5), *c* = 23.220 (4) Å, β = 97.22 (2)°, *M* = 485.5, *Z* = 8, *D*_x = 1.29 g cm⁻³. The deviations from an idealized trigonal bipyramidal geometry for this phosphorane bridgehead with two fused five-membered rings may be interpreted in terms of a 15% translation between a system with a joint equatorial P–N bond and that with a joint axial bond. Planarity of the equatorial atoms is retained. Two significantly different P–O_{ax} lengths of 1.763 (5) and 1.700 (5) and a long P–N_{eq} distance of 1.703 (6) Å are observed.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex *P*2₁ four-circle diffractometer (Mo *K*α, 0.71069 Å). Intensities from a prismatic crystal, 0.16 × 0.30 × 0.18 mm, were collected on the diffractometer with graphite-monochromated Mo *K*α radiation. Measurements were carried out in the θ–2θ mode (3.0 ≤ 2θ ≤ 50.0°) at scan speeds varying linearly between 2.93° min⁻¹ (150 c.p.s. and below) and 9.77° min⁻¹ (5000 c.p.s. and above). Scan and background times were equal. Three standard reflexions, monitored at regular intervals, did not display any significant variations. Lorentz and polarization but no absorption [$\mu(\text{Mo } K\alpha) = 1.01 \text{ cm}^{-1}$] corrections were applied. After application of the rejection criterion $F \geq 2.5\sigma(F)$, where $\sigma(F)$ is based on counting statistics, averaging of equivalencies yielded 2402 independent reflexions for use in the analysis.

The structure was solved by a multiresolution technique (Sheldrick, 1976) in which 2¹² sign permutations were expanded by the Σ₂ formula. A permutation is rejected in this method if its internal consistency falls at any stage below a preset value. Additionally, a similarity test is applied to avoid the calculation of too many closely similar *E* maps. In this case, four *E* maps were computed, of which the best (in terms of Σ₂ consistency) revealed the positions of 27 of the 36 heavy atoms. Refinement was carried out by block-diagonal least squares minimizing Σ*w*Δ². The coordinates of the H atoms were subsequently revealed by difference syntheses and included in the final cycles of refinement. Group isotropic temperature factors were introduced for the H atoms of each phenyl group. The final value of $R_G = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$ was 0.075, with $R_w = \sum w^{1/2}\Delta / \sum w^{1/2}F_o = 0.065$ and $R = 0.065$. The weights were given by $w = k / (\sigma^2(F_o) + gF_o^2)$ where *k* and *g* refined to 2.6618

and 0.000644 respectively. A final difference synthesis displayed no peaks or troughs of electron density greater than 0.44 e Å⁻³. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed. The heavy-atom coordinates are listed in Table 1 and their anisotropic temperature-factor components in Table 2; the H atom positional parameters are summarized in Table 3. The full covariance matrix was used in the estimation of the bond lengths and selected angles presented in Tables 4–6.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31486 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atom positional parameters ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
P	3735 (1)	–900 (2)	6503 (1)
O(1)	4345 (1)	–1685 (4)	6831 (1)
O(2)	3125 (1)	–373 (4)	6127 (1)
N	3915 (1)	–1496 (4)	5826 (1)
C(11)	4648 (2)	–2369 (6)	6462 (2)
C(12)	5141 (2)	–3077 (6)	6627 (2)
C(13)	5404 (2)	–3736 (6)	6199 (3)
C(14)	5179 (2)	–3702 (7)	5625 (3)
C(15)	4675 (2)	–2964 (6)	5456 (2)
C(16)	4421 (2)	–2295 (5)	5883 (2)
C(2)	3100 (2)	–444 (5)	5532 (2)
C(21)	2589 (2)	161 (5)	5218 (2)
C(22)	2264 (2)	1101 (6)	5508 (2)
C(23)	1765 (2)	1625 (7)	5238 (3)
C(24)	1585 (2)	1221 (8)	4679 (3)
C(25)	1898 (2)	306 (7)	4390 (2)
C(26)	2398 (2)	–240 (7)	4653 (2)
C(3)	3544 (2)	–1072 (5)	5359 (2)
C(31)	3702 (2)	–1257 (5)	4769 (2)
C(32)	3508 (2)	–2438 (6)	4411 (2)
C(33)	3668 (2)	–2580 (8)	3864 (2)
C(34)	4022 (3)	–1547 (9)	3672 (3)
C(35)	4217 (2)	–374 (8)	4025 (3)
C(36)	4057 (2)	–216 (7)	4572 (2)
C(41)	3365 (2)	–1869 (6)	7026 (2)
C(42)	3552 (2)	–1833 (7)	7616 (2)
C(43)	3283 (3)	–2629 (8)	8004 (2)
C(44)	2840 (2)	–3517 (8)	7812 (3)
C(45)	2646 (2)	–3566 (8)	7236 (3)
C(46)	2901 (2)	–2723 (7)	6846 (2)
C(51)	3935 (2)	1011 (7)	6725 (2)
C(52)	3599 (3)	1968 (9)	6975 (3)
C(53)	3748 (3)	3435 (9)	7126 (3)
C(54)	4229 (4)	3962 (10)	7007 (4)
C(55)	4578 (5)	3016 (15)	6781 (9)
C(56)	4425 (3)	1580 (11)	6608 (4)

Table 2. Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)

The anisotropic temperature factor takes the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	35 (1)	69 (1)	39 (1)	0 (1)	0 (1)	6 (1)
O(1)	42 (2)	106 (3)	47 (2)	8 (2)	-1 (2)	20 (2)
O(2)	41 (2)	81 (3)	33 (2)	1 (2)	3 (1)	13 (2)
N	34 (2)	72 (3)	43 (2)	0 (2)	-1 (2)	10 (2)
C(11)	40 (3)	62 (4)	56 (3)	1 (3)	0 (2)	-1 (3)
C(12)	39 (3)	76 (4)	65 (3)	12 (3)	-2 (3)	8 (3)
C(13)	42 (3)	71 (4)	95 (4)	-1 (3)	-7 (3)	11 (3)
C(14)	50 (3)	83 (5)	87 (4)	-28 (4)	4 (3)	9 (3)
C(15)	49 (3)	77 (4)	62 (3)	-19 (3)	-2 (3)	10 (3)
C(16)	37 (2)	59 (3)	50 (3)	-4 (3)	-1 (2)	-1 (2)
C(2)	38 (3)	52 (3)	40 (3)	-3 (2)	2 (2)	0 (2)
C(21)	36 (3)	49 (3)	38 (3)	3 (2)	1 (2)	0 (2)
C(22)	50 (3)	70 (4)	45 (3)	2 (3)	1 (2)	8 (3)
C(23)	56 (3)	80 (4)	70 (4)	6 (3)	2 (3)	3 (3)
C(24)	48 (3)	89 (5)	73 (4)	11 (4)	-12 (3)	16 (3)
C(25)	63 (4)	97 (5)	58 (3)	-9 (4)	-20 (3)	15 (4)
C(26)	54 (3)	84 (4)	49 (3)	-12 (3)	-6 (3)	17 (3)
C(3)	37 (2)	49 (3)	38 (2)	2 (2)	-1 (2)	1 (2)
C(31)	37 (2)	39 (3)	44 (3)	2 (2)	4 (2)	1 (2)
C(32)	48 (3)	60 (4)	51 (3)	-6 (3)	3 (3)	-4 (3)
C(33)	68 (4)	90 (5)	51 (4)	-19 (4)	3 (3)	10 (4)
C(34)	92 (5)	107 (6)	50 (4)	15 (4)	28 (3)	25 (5)
C(35)	79 (4)	72 (5)	90 (5)	17 (4)	44 (3)	2 (4)
C(36)	54 (3)	61 (4)	62 (4)	1 (1)	15 (3)	0 (3)
C(41)	38 (3)	71 (4)	44 (3)	2 (2)	1 (2)	10 (3)
C(42)	54 (3)	92 (5)	47 (3)	7 (3)	3 (3)	1 (3)
C(43)	69 (4)	133 (6)	47 (3)	17 (4)	4 (3)	9 (4)
C(44)	63 (4)	106 (6)	79 (5)	28 (4)	22 (3)	5 (4)
C(45)	64 (4)	98 (5)	79 (5)	4 (4)	13 (4)	-7 (4)
C(46)	55 (3)	88 (5)	51 (3)	-5 (3)	7 (3)	-2 (3)
C(51)	40 (3)	77 (4)	46 (3)	-5 (3)	-4 (2)	-1 (3)
C(52)	60 (4)	71 (5)	90 (5)	-7 (4)	11 (4)	-2 (4)
C(53)	93 (5)	74 (6)	83 (5)	-8 (4)	7 (4)	9 (4)
C(54)	112 (6)	70 (6)	135 (7)	-21 (6)	10 (5)	-13 (6)
C(55)	120 (8)	128 (10)	331 (18)	-85 (11)	82 (9)	-50 (7)
C(56)	71 (3)	112 (4)	239 (3)	-81 (3)	58 (2)	-32 (3)

Table 3. Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
H(12)	5268 (17)	-3075 (50)	7052 (19)	68 (7)
H(13)	5738 (18)	-4284 (52)	6287 (18)	68 (7)
H(14)	5387 (17)	-4035 (53)	5336 (19)	68 (7)
H(15)	4536 (17)	-3016 (52)	5055 (18)	68 (7)
H(22)	2401 (19)	1306 (58)	5904 (20)	86 (8)
H(23)	1573 (20)	2367 (59)	5461 (21)	86 (8)
H(24)	1233 (20)	1623 (63)	4515 (21)	86 (8)
H(25)	1769 (20)	-1 (57)	3996 (23)	86 (8)
H(26)	2604 (20)	-730 (61)	4437 (21)	86 (8)
H(32)	3282 (20)	-3135 (58)	4556 (20)	84 (8)
H(33)	3548 (20)	-3461 (58)	3620 (21)	84 (8)
H(34)	4151 (20)	-1505 (60)	3301 (21)	84 (8)
H(35)	4468 (21)	388 (60)	3889 (22)	84 (8)
H(36)	4204 (20)	527 (61)	4831 (21)	84 (8)
H(42)	3854 (20)	-1212 (60)	7729 (21)	86 (8)
H(43)	3419 (20)	-2473 (56)	8409 (22)	86 (8)
H(44)	2668 (20)	-4083 (62)	8073 (21)	86 (8)
H(45)	2342 (20)	-4310 (63)	7092 (21)	86 (8)
H(46)	2782 (20)	-2686 (58)	6454 (21)	86 (8)
H(52)	3231 (32)	1556 (105)	6999 (35)	111 (17)
H(53)	3513 (32)	4085 (94)	7327 (31)	111 (17)
H(54)	4330 (32)	4985 (85)	7118 (32)	111 (17)
H(55)	4657 (39)	3506 (130)	6544 (50)	111 (17)
H(56)	4709 (29)	936 (91)	6395 (30)	111 (17)

Table 4. Bond lengths (\AA)

P—O(1)	1.763 (5)	P—O(2)	1.700 (5)
P—C(41)	1.818 (5)	P—C(51)	1.811 (6)
P—N	1.703 (6)	C(2)—C(3)	1.329 (5)
O(1)—C(11)	1.347 (8)	O(2)—C(2)	1.376 (5)
N—C(16)	1.421 (8)	N—C(3)	1.427 (5)
C(11)—C(12)	1.373 (10)	C(12)—C(13)	1.381 (11)
C(13)—C(14)	1.376 (12)	C(14)—C(15)	1.411 (11)
C(15)—C(16)	1.370 (10)	C(16)—C(11)	1.391 (9)
C(2)—C(21)	1.470 (5)	C(3)—C(31)	1.479 (5)
C(21)—C(22)	1.383 (6)	C(22)—C(23)	1.385 (6)
C(23)—C(24)	1.365 (7)	C(24)—C(25)	1.350 (8)
C(25)—C(26)	1.387 (7)	C(26)—C(27)	1.381 (6)
C(31)—C(32)	1.380 (6)	C(32)—C(33)	1.383 (7)
C(33)—C(34)	1.374 (9)	C(34)—C(35)	1.368 (9)
C(35)—C(36)	1.382 (8)	C(36)—C(31)	1.383 (6)
C(41)—C(42)	1.390 (6)	C(42)—C(43)	1.374 (7)
C(43)—C(44)	1.369 (8)	C(44)—C(45)	1.363 (8)
C(45)—C(46)	1.381 (7)	C(46)—C(41)	1.385 (6)
C(51)—C(52)	1.361 (8)	C(52)—C(53)	1.376 (10)
C(53)—C(54)	1.330 (10)	C(54)—C(55)	1.350 (15)
C(55)—C(56)	1.367 (14)	C(56)—C(51)	1.362 (8)

Table 5. Bond lengths (\AA) to hydrogen atoms

C(12)—H(12)	1.00 (7)	C(13)—H(13)	0.95 (7)
C(14)—H(14)	0.94 (7)	C(15)—H(15)	0.95 (7)
C(22)—H(22)	0.96 (5)	C(23)—H(23)	0.99 (5)
C(24)—H(24)	0.97 (5)	C(25)—H(25)	0.97 (5)
C(26)—H(26)	0.87 (5)	C(32)—H(32)	0.92 (5)
C(33)—H(33)	0.98 (5)	C(34)—H(34)	0.94 (5)
C(35)—H(35)	0.99 (5)	C(36)—H(36)	0.93 (5)
C(42)—H(42)	0.93 (5)	C(43)—H(43)	0.97 (5)
C(44)—H(44)	0.93 (5)	C(45)—H(45)	1.02 (5)
C(46)—H(46)	0.92 (5)	C(52)—H(52)	0.98 (8)
C(53)—H(53)	0.97 (7)	C(54)—H(54)	0.96 (7)
C(55)—H(55)	0.74 (12)	C(56)—H(56)	1.07 (7)

Table 6. Bond angles ($^\circ$)

O(1)—P—O(2)	171.6 (3)	O(1)—P—N	87.6 (3)
O(1)—P—C(41)	89.7 (4)	O(1)—P—C(51)	93.3 (4)
O(2)—P—N	86.6 (3)	O(2)—P—C(41)	89.4 (4)
O(2)—P—C(51)	94.7 (4)	N—P—C(41)	130.6 (4)
N—P—C(51)	116.5 (4)	C(41)—P—C(51)	112.8 (5)
C(11)—O(1)—P	114.4 (4)	C(2)—O(2)—P	115.5 (4)
C(16)—N—P	115.9 (4)	C(3)—N—P	114.9 (4)
O(1)—C(11)—C(16)	114.1 (6)	O(2)—C(2)—C(3)	112.7 (4)
C(11)—C(16)—N	108.0 (6)	C(2)—C(3)—N	109.3 (4)
C(16)—N—C(3)	129.2 (5)		

Discussion. In recent years there has been a sizeable increase in the number of known phosphoranes, their stability being normally attributable to the incorporation of P into one or two small rings, which for a trigonal bipyramidal geometry always arrange themselves in an axial-equatorial conformation in order to minimize ring strain. For bicyclophosphoranes, which contain fused rings, two such conformations are possible, namely with a joint equatorial or with a joint axial bond. Previous structural determinations of a phosphorane bridgehead of fused five- and four-membered (Kabachnik, Gilyarov, Tikhonina, Kalinin, Andrianov, Struchkov & Timofeeva, 1974) and five- and six-membered rings (Swank, Caughlan, Ramirez &

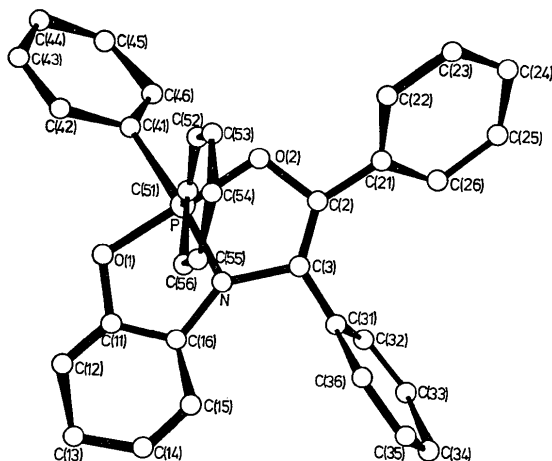


Fig. 1. Atom numbering in the molecule.

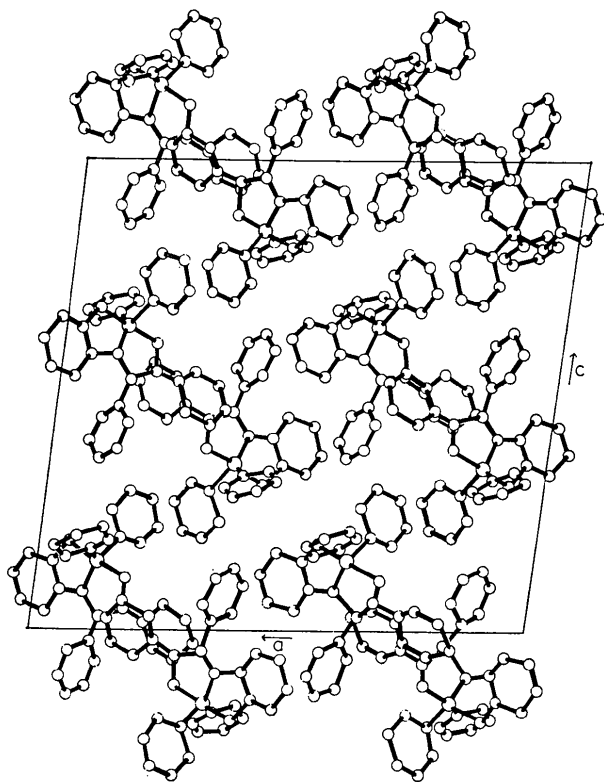


Fig. 2. Projection of the structure perpendicular to [010].

Pilot, 1971) have shown that these take up the former conformation. This work describes the structure of a phosphorane with two fused five-membered rings, a preliminary report of which has already appeared

(Sheldrick, Schmidpeter & Weinmaier, 1975). As for the other examples of bicyclic systems, the structure alternative with equatorial annelation is approximately fulfilled, although the distortion of the angles of the trigonal bipyramid can be interpreted in terms of a 15% pseudorotation towards the second conformation about P–C(51) (Fig. 1) as a pivot. Thus, C(51)–P–O(1) and C(51)–P–O(2) increase to 93.3 (4) and 94.7 (4)° [theoretical value for a 15% transition = 94.5°]. N–P–C(41) increases to 130.6 (4) [129°] while the other two 'equatorial' angles accordingly decrease, and O(1)–P–O(2) decreases to 171.6 (3) [171°]. In agreement with this model is the long P–N_{eq} distance of 1.703 (6) which compares with values of 1.59–1.64 Å observed in the diphosphetidines (Sheldrick & Hewson, 1975). Whereas P as one of the bridgeheads of the bicyclic system is located outside the plane of the surrounding ring members, the other bridgehead N is in a planar environment. This is possible because, while the benzo-oxazaphospholine ring P–O(1)–C(11)–C(16)–N forms a good plane which also approximately contains C(3), the other five-membered ring exhibits an envelope configuration with P lying 0.19 Å outside the plane O(2)–C(2)–C(3)–N. A remarkable difference is to be observed between the phenolic P–O(1) (1.763) and the enolic P–O(2) bond (1.700 Å) which suggests that the former bond contains less (*p* → *d*) π bonding character as a result of interaction of the O 2*p*-orbitals with the π-system of the benzene ring.

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