Crystal and Molecular Structure of a New Eight-membered Tetraphospha-macrocycle, $(-\overline{\mathrm{PCPh{=}CMeCMe{=}C}}-)_4$ †

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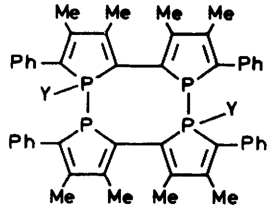
A new P_4C_4 eight-membered macrocycle has been obtained in one step from 3,4-dimethyl-1-phenylphosphole. A comparison of the *X*-ray crystal structure of this P_4C_4 macrocycle with that of its decacarbonyldimolybdenum complex shows that the P_4C_4 crown gains a very high flexibility through an easy rotation of the adjacent phospholyl units round the C–C and P–P bonds of the central eight-membered ring. This means that this P_4C_4 macrocycle can adapt its shape to the stereochemical requirements of the complexed metals. The P–P and C–C bonds of the crown [average 2.191(3) and 1.47(1) Å respectively] are significantly shorter than normal P–P and C–C single bonds. Thus some conjugative interactions probably exist between the adjacent phospholyl rings. These interactions are suppressed in the decacarbonyldimolybdenum complex.

Polyphospha-macrocycles are currently under active investigation [1–13] because of their possible uses as transition metal ligands in co-ordination chemistry. However, such studies are hampered by long and tedious synthetic procedures. In this context, the discovery of a direct one-step synthesis of the P_4C_4 crown (1) by thermal tetramerization of 3,4-dimethyl-1-phenylphosphole is especially noteworthy.[14] It is possible



(1); Y = lone pair
(2); Y = Mo(CO)$_5$

either to insert ' spacers ' within the P–P bonds of (1) in order to obtain a whole range of new tetraphospha-macrocycles or to use (1) directly as a ligand in co-ordination chemistry. For such a use, the flexibility of the P_4C_4 ring of (1) is a key parameter. In order to evaluate this flexibility, we have performed a *X*-ray crystal structure analysis of (1) and compared the results thus obtained with those obtained in our previous study [14] on the structure of the decacarbonyldimolybdenum complex of this macrocycle, (2).

Experimental

Suitable single crystals of (1) were obtained by slow evaporation at room temperature of chlorobenzene solutions. The methods used for the determination of the crystal system and the unit-cell dimensions have been described elsewhere.[15]

Crystal Data.—$C_{48}H_{44}P_4$, $M = 744.8$, Triclinic, $a = 11.615(4)$, $b = 14.997(4)$, $c = 23.050(8)$ Å, $\alpha = 90.18(2)$, $\beta = 92.42(2)$, $\gamma = 72.70(2)°$, $U = 4\,006$ Å^3, $D_m = 1.20 \pm 0.02$, $Z = 4$, $D_c = 1.235$ g cm^{-3}, $F(000) = 1\,568$, space group $P\bar{1}$, $\mu(\text{Mo-}K_\alpha) = 19.64$ cm^{-1}, $\lambda = 0.7107$ Å.

A crystal of 0.20 × 0.22 × 0.18 mm was sealed in a Lindemann glass capillary. All quantitative data were obtained from a CAD4-F four-circle diffractometer using the method outlined elsewhere.[15] A total of 6 914 hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ reflections were prescanned ($6 < \theta < 50°$). A unique data set of 3 053 reflections having $I > 3\sigma(I)$ was used for refining the structure.

The structure was solved using MULTAN.[16] Hydrogen atoms were introduced in structure factor calculations by their computed co-ordinates (C–H = 0.95 Å) and isotropic thermal parameters ($B_H = 8$ Å^2) but not refined. Full-matrix least-squares refinement converged to $R(F)$ 0.089 and $R'(F)$ 0.109. The unit weight observation was 1.99 with $p = 0.08$ in $\sigma^2(F^2) = \sigma^2_{\text{count}} + (pI)^2$. Due to the presence of numerous chemically equivalent units, relatively good averages can be determined, despite the poor quality of the diffraction data.

Discussion

Table 1 gives selected lengths and angles as well as significant averages. Table 2 lists selected dihedral and torsional angles.

In the crystalline state, there are two molecules of (1) in the asymmetric unit. Each molecule may be viewed either as a tetramer of the phospholyl moiety (3), or as a dimer of the 2,2'-biphospholyl moiety (4), or as a dimer of the 1,1'-biphospholyl moiety (5). We shall discuss the structure of (1) from all these points of view.

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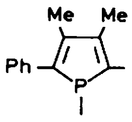
† 1,2,7,8,9,10,15,16-Octamethyl-3,6,11,14-tetraphenyltetraphospholo[1,2-*b*;2',1'-*d*;1'',2''-*f*;2''',1'''-*h*][1,2,5,6]tetraphosphocin.

Supplementary data available (No. SUP 23523, 22 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

P(1)-P(3)	2.198(6)	C(1)-C(2)	1.36(2)
P(2)-P(4)	2.191(6)	C(3)-C(4)	1.34(2)
P(5)-P(7)	2.201(6)	C(7)-C(8)	1.38(2)
P(6)-P(8)	2.175(6)	C(9)-C(10)	1.41(2)
P-P mean	2.191(3)	C(25)-C(26)	1.33(2)
		C(27)-C(28)	1.35(2)
P(1)-C(1)	1.72(2)	C(31)-C(32)	1.44(2)
P(1)-C(4)	1.78(2)	C(33)-C(34)	1.33(2)
P(2)-C(7)	1.79(1)	C(49)-C(50)	1.33(2)
P(2)-C(10)	1.76(2)	C(51)-C(52)	1.39(2)
P(3)-C(25)	1.83(2)	C(55)-C(56)	1.38(2)
P(3)-C(28)	1.78(2)	C(57)-C(58)	1.43(2)
P(4)-C(31)	1.74(2)	C(73)-C(74)	1.35(2)
P(4)-C(34)	1.79(2)	C(75)-C(76)	1.37(2)
P(5)-C(49)	1.86(2)	C(79)-C(80)	1.37(2)
P(5)-C(52)	1.76(2)	C(81)-C(82)	1.40(2)
P(6)-C(55)	1.82(2)	C-C mean	1.374(6) [a]
P(6)-C(58)	1.77(2)		
P(7)-C(73)	1.79(2)	Mean bond distances [b]	
P(7)-C(76)	1.79(2)	C(p.r.)-C(methyl)	1.495(6)
P(8)-C(79)	1.77(2)	C(p.r.)-C(phenyl)	1.449(9)
P(8)-C(82)	1.79(2)	C-C(phenyl)	1.381(4)
P-C mean	1.785(5)		
		Mean bond angles	
C(4)-C(7)	1.44(2)	C(p.r.)-P-C(p.r.)	91.8(4)
C(25)-C(31)	1.51(2)	P-C(p.r.)-C(p.r.)	109.2(4)
C(52)-C(55)	1.48(2)	P-C(p.r.)-C′(p.r.) [c]	122.9(5)
C(76)-C(79)	1.45(2)	P-C(p.r.)-C(phenyl)	120.5(6)
C-C mean	1.47(1) [d]	C-C-C(p.r.)	114.2(5)
C(2)-C(3)	1.45(2)		
C(8)-C(9)	1.40(2)		
C(26)-C(27)	1.45(2)		
C(32)-C(33)	1.48(2)		
C(50)-C(51)	1.42(2)		
C(56)-C(57)	1.46(2)		
C(74)-C(75)	1.44(2)		
C(80)-C(81)	1.43(2)		
C-C mean	1.442(8) [e]		

[a] C^{α}–C^{β} bonds of phospholyl rings. [b] p.r. = Phospholyl ring. [c] Primed atom indicates adjacent ring. [d] Bonds between phospholyl rings. [e] C^{β}–$C^{\beta'}$ bonds of phospholyl rings.



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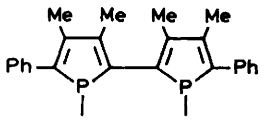

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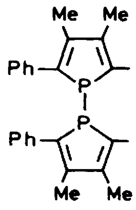

(5)

Table 2. Selected dihedral and torsional angles (°)

	Folding angle ($C^{\alpha}\cdots C^{\alpha'}$ axis) [a]	Distance (Å) of P to mean plane of C moiety of ring
Ring 1.	10.5	0.225(4)
Ring 2.	9.8	0.208(5)
Ring 3.	8.3	0.182(5)
Ring 4.	10.1	0.217(4)
Ring 5.	10.1	0.221(4)
Ring 6.	9.3	0.200(5)
Ring 7.	12.6	0.268(5)
Ring 8.	10.9	0.231(4)
Dihedral angles		
C(1)—C(4)/C(7)-C(10)		47.9
C(25)—C(28)/C(31)—C(34)		44.5
C(49)—C(52)/C(55)—C(58)		45.1
C(73)—C(76)/C(79)—C(82)		50.2
C(1)—C(4)/C(13)—C(18) [b]		40.0
C(7)—C(10)/C(19)—C(24) [b]		38.8
C(25)—C(28)/C(37)—C(42) [b]		41.1
C(31)—C(34)/C(43)—C(48) [b]		40.5
C(49)—C(52)/C(61)—C(66) [b]		40.8
C(55)—C(58)/C(67)—C(72) [b]		44.7
C(73)—C(76)/C(85)—C(90) [b]		42.4
C(79)—C(82)/C(91)—C(96) [b]		38.5
Torsional angles		
P(1)-C(4)-C(7)-P(2)		140(1)
P(3)-C(25)-C(31)-P(4)		143(1)
P(5)-C(52)-C(55)-P(6)		−143(1)
P(7)-C(76)-C(79)-P(8)		−139(1)
C(4)-P(1)-P(3)-C(25)		8(1)
C(7)-P(2)-P(4)-C(31)		7(1)
C(52)-P(5)-P(7)-C(76)		−7(1)
C(55)-P(6)-P(8)-C(79)		−7(1)
C(4)-P(1)-P(3)-C(28)		104(1)
C(7)-P(2)-P(4)-C(34)		102(1)
C(7)-C(4)-P(1)-P(3)		−66(1)
C(31)-C(25)-P(3)-P(1)		−59(1)
C(4)-C(7)-P(2)-P(4)		−59(1)
C(25)-C(31)-P(4)-P(2)		−69(1)
C(55)-C(52)-P(5)-P(7)		68(1)
C(79)-C(76)-P(7)-P(5)		60(1)
C(52)-C(55)-P(6)-P(8)		60(1)
C(76)-C(79)-P(8)-P(6)		64(1)
C(52)-P(5)-P(7)-C(73)		−104(1)
C(55)-P(6)-P(8)-C(82)		−105(1)

[a] See Figure 1 for numbering of phospholyl rings. [b] Phenyl rings.

Table 3. Structural comparison between 1-benzylphosphole and the phospholyl moieties of (1)

	1-Benzyl-phosphole *	(1)
Intracyclic P-C bond length (average) (Å)	1.783	1.785
C^{β}-$C^{\beta'}$ bond length (Å)	1.438	1.442 (average)
C^{α}-C^{β} bond length (average) (Å)	1.343	1.374
Intracyclic CPC bond angle (°)	90.7	91.8 (average)
Ring folding angle (°)	9.6	8.3—12.6

* Data from ref. 17.

Table 3 compares the average structure of phospholyl group (3) with the structure of 1-benzylphosphole.[17]

The close similarity between the two sets of data is obvious. The incorporation of (3) into a tetramer does not affect its

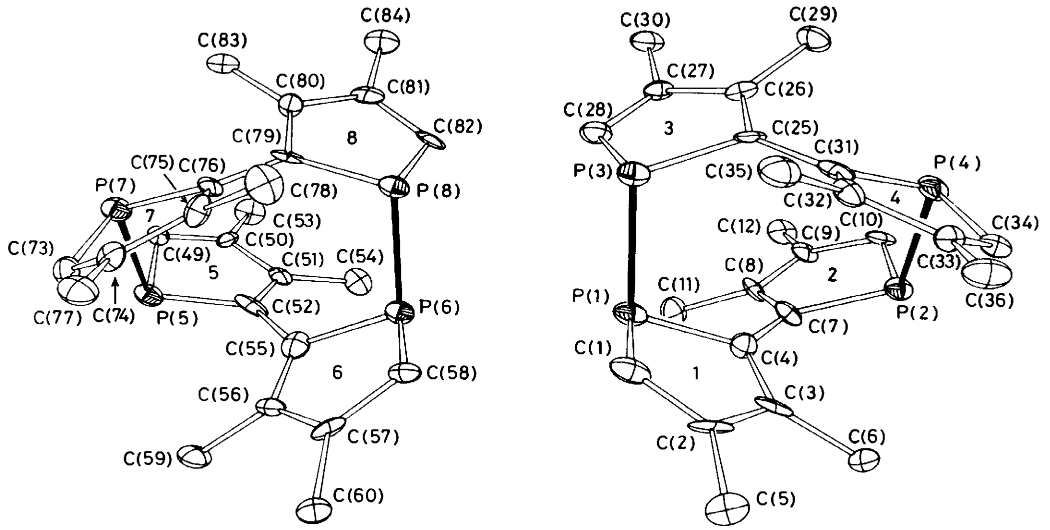

Figure 1. ORTEP plot of the two P_4C_4 crowns. Ellipsoids are scaled to enclose 40% of the electronic density; phenyl rings and hydrogen atoms are omitted for clarity

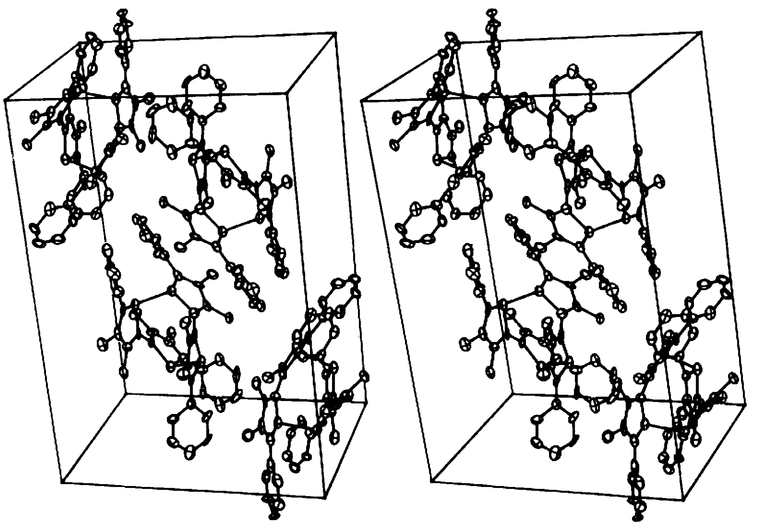

Figure 2. ORTEP stereopair plot of the unit-cell contents (directions: *a* horizontal, *c* vertical, and viewed along *b*)

structure. The weak aromaticity of the phosphole ring is retained (for a discussion, see ref. 18).

The most important feature of the 2,2′-biphospholyl units (4) in (1) is that their two phosphorus atoms are *trans* with respect to the C–C bond linking the two phosphole rings whereas in complex (2),[14] the two corresponding phosphorus atoms are *cis* with respect to the same bond. As reported in Table 2 the absolute values of the P–C–C–P torsion angles lie in the range 139—143°, whereas in (2) this angle is 44.2°. As a consequence, the P–P distance in (4) has a mean value of 4.437 Å compared to 3.565 Å in (2).

Thus, the P_4C_4 crown gains much flexibility through the easy rotation of the phospholyl units around their C–C bridges. In the same way, the relative orientations around the P–P bridges of the two phospholyl moieties within the 1,1′-biphospholyl units (5) are considerably different in (1) and (2). The absolute values of the appropriate C–P–P–C torsion angles lie in the range 102—105° in (1) (Table 2), whereas in (2) a corresponding angle such as C(1)–P(1)–P(2′)–C(7′) is 3.7° (for the numbering scheme, see Figure 1 of ref. 14). Thus the P_4C_4 crown gains additional flexibility around the P–P bridges.

The very high flexibility of this P_4C_4 macrocycle means that it will easily adapt its overall shape to the stereochemical requirements of the metals to which it is complexed. Thus, it should have great potential in co-ordination chemistry.

Figure 1 shows the skeleton of two P_4C_4 crowns in the asymmetric unit and Figure 2 a stereopair of the unit-cell contents. In (1) this P_4C_4 crown has no symmetry element, whereas in (2) it has a crystallographic two-fold axis. This again underlines the high flexibility of the eight-membered ring.

The non-bonded opposite P–P distances in (1) are similar (mean value 4.882 Å) whereas in (2), two types of these P–P distances were found: 3.303 and 4.506 Å. This is a consequence of the different relative positions of the phosphorus atoms in (1) and (2).

The two moieties (4) of the P_4C_4 crown containing atoms

Table 4. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
P(1)	0.630 6(4)	0.226 5(3)	0.097 8(2)	C(45)	0.942(2)	0.057 4(11)	0.405 5(9)
P(2)	0.571 4(4)	0.134 6(3)	0.276 6(2)	C(46)	0.880(2)	0.013 4(11)	0.446 8(8)
P(3)	0.573 4(4)	0.092 0(3)	0.067 2(2)	C(47)	0.775(1)	−0.030 4(9)	0.427 6(8)
P(4)	0.613 3(4)	−0.000 1(3)	0.250 1(2)	C(48)	0.738(1)	−0.036 3(10)	0.371 9(8)
P(5)	0.613 5(4)	0.500 0(3)	0.254 9(2)	C(49)	0.771(2)	0.504 5(9)	0.242 3(7)
P(6)	0.571 5(4)	0.592 8(3)	0.435 6(2)	C(50)	0.823(1)	0.497 6(9)	0.294 3(7)
P(7)	0.568 7(4)	0.634 8(3)	0.227 2(2)	C(51)	0.756(2)	0.499 0(9)	0.344 2(7)
P(8)	0.625 0(4)	0.727 3(3)	0.409 6(2)	C(52)	0.640(1)	0.508 2(9)	0.330 8(8)
C(1)	0.778(1)	0.229 2(10)	0.090 1(8)	C(53)	0.952(2)	0.484 5(13)	0.302 3(9)
C(2)	0.840(1)	0.242 0(9)	0.141 4(8)	C(54)	0.808(2)	0.492 5(11)	0.404 3(8)
C(3)	0.763(1)	0.236 8(8)	0.189 9(8)	C(55)	0.546(2)	0.523 3(11)	0.370 9(8)
C(4)	0.651(1)	0.221 3(10)	0.175 0(7)	C(56)	0.340(1)	0.499 5(9)	0.365 5(8)
C(5)	0.962(2)	0.266 9(12)	0.148 0(9)	C(57)	0.356(1)	0.541 1(10)	0.406 5(7)
C(6)	0.818(2)	0.249 6(11)	0.251 7(8)	C(58)	0.421(1)	0.600 8(10)	0.445 2(7)
C(7)	0.559(1)	0.204 3(9)	0.213 7(7)	C(59)	0.383(2)	0.429 3(11)	0.322 6(9)
C(8)	0.445(1)	0.226 2(9)	0.205 2(7)	C(60)	0.234(1)	0.512 1(12)	0.405 7(8)
C(9)	0.368(1)	0.186 3(9)	0.243 9(8)	C(61)	0.804(1)	0.507 2(9)	0.185 6(7)
C(10)	0.421(1)	0.124 9(10)	0.281 9(8)	C(62)	0.745(1)	0.467 8(10)	0.137 5(7)
C(11)	0.402(2)	0.296 9(12)	0.164 5(8)	C(63)	0.782(2)	0.467 4(10)	0.081 3(8)
C(12)	0.243(1)	0.205 8(10)	0.244 8(9)	C(64)	0.879(2)	0.516 0(11)	0.070 8(10)
C(13)	0.823(1)	0.226 7(10)	0.030 3(10)	C(65)	0.943(1)	0.558 5(11)	0.114 7(8)
C(14)	0.766(2)	0.262 4(11)	−0.019 0(9)	C(66)	0.908(2)	0.556 6(10)	0.168 6(7)
C(15)	0.804(2)	0.255 5(13)	−0.070 8(8)	C(67)	0.380(1)	0.655 6(9)	0.490 6(8)
C(16)	0.905(2)	0.214 1(12)	−0.087 0(8)	C(68)	0.285(2)	0.702 2(11)	0.478 0(8)
C(17)	0.961(2)	0.179 8(12)	−0.037 3(9)	C(69)	0.239(2)	0.761 7(12)	0.516 1(8)
C(18)	0.924(2)	0.184 3(11)	0.017 1(9)	C(70)	0.291(1)	0.772 7(9)	0.569 5(8)
C(19)	0.369(1)	0.066 6(10)	0.327 2(8)	C(71)	0.387(2)	0.726 5(11)	0.584 6(7)
C(20)	0.424(2)	0.055 9(11)	0.379 4(9)	C(72)	0.435(1)	0.667 5(10)	0.544 5(8)
C(21)	0.381(2)	0.000 6(14)	0.420 3(9)	C(73)	0.415(2)	0.622 7(11)	0.214 8(8)
C(22)	0.272(2)	−0.042 5(12)	0.409 8(9)	C(74)	0.366(1)	0.683 3(10)	0.248 4(7)
C(23)	0.216(2)	−0.032 3(12)	0.360 1(9)	C(75)	0.442(1)	0.725 1(12)	0.292 1(7)
C(24)	0.257(1)	0.025 6(10)	0.316 8(9)	C(76)	0.555(1)	0.702 7(9)	0.290 2(7)
C(25)	0.546(1)	0.022 7(9)	0.131 0(8)	C(77)	0.241(2)	0.705 5(10)	0.244 0(9)
C(26)	0.432(1)	0.003 0(9)	0.130 2(8)	C(78)	0.397(2)	0.797 8(12)	0.331 9(9)
C(27)	0.362(1)	0.047 5(9)	0.086 8(7)	C(79)	0.646(1)	0.723 0(8)	0.334 1(7)
C(28)	0.423(2)	0.101 4(11)	0.051 5(7)	C(80)	0.760(1)	0.740 5(10)	0.324 5(7)
C(29)	0.376(2)	−0.067 8(12)	0.170 3(9)	C(81)	0.834(1)	0.748 2(9)	0.376 3(8)
C(30)	0.239(2)	0.023 3(10)	0.079 4(9)	C(82)	0.777(2)	0.732 8(9)	0.428 1(8)
C(31)	0.640(1)	0.007 3(9)	0.176 5(8)	C(83)	0.815(2)	0.751 1(11)	0.267 5(9)
C(32)	0.760(1)	−0.004 8(9)	0.164 9(7)	C(84)	0.962(2)	0.774 5(12)	0.376 2(9)
C(33)	0.825(1)	−0.008 0(10)	0.221 2(7)	C(85)	0.361(1)	0.567 4(11)	0.170 9(7)
C(34)	0.765(1)	0.001 1(9)	0.268 5(7)	C(86)	0.252(1)	0.518 8(10)	0.174 0(9)
C(35)	0.806(2)	−0.016 5(11)	0.110 6(9)	C(87)	0.217(2)	0.464 8(11)	0.123 7(9)
C(36)	0.951(2)	−0.021 0(12)	0.217 5(9)	C(88)	0.277(2)	0.459 7(13)	0.075 6(8)
C(37)	0.380(1)	0.159 6(10)	0.003 8(7)	C(89)	0.380(2)	0.505 2(13)	0.076 0(11)
C(38)	0.283(2)	0.207 1(10)	0.011 2(8)	C(90)	0.417(2)	0.557 8(10)	0.120 9(8)
C(39)	0.246(2)	0.263 6(11)	−0.033 4(9)	C(91)	0.818(1)	0.731 7(9)	0.488 1(8)
C(40)	0.307(2)	0.274 1(11)	−0.084 7(8)	C(92)	0.755(1)	0.767 1(10)	0.530 9(8)
C(41)	0.406(2)	0.227 7(10)	−0.089 6(8)	C(93)	0.791(2)	0.765 4(10)	0.589 7(8)
C(42)	0.440(1)	0.169 9(10)	−0.046 5(7)	C(94)	0.893(1)	0.726 6(11)	0.605 9(8)
C(43)	0.807(1)	0.005 5(9)	0.328 3(8)	C(95)	0.963(1)	0.693 4(12)	0.562 0(9)
C(44)	0.910(1)	0.050 2(10)	0.348 4(7)	C(96)	0.921(1)	0.697 2(10)	0.506 2(8)

P(1)—P(4) are superposable, as are those of the P_4C_4 crown P(5)—P(8), but one moiety (4) of the first crown is not superposable on one of the second crown. Using program COMPAR,* which attempts to superpose two molecules or fragments of molecules by a least-squares procedure, it has been found that the two crystallographically independent P_4C_4 crowns are not identical, but are enantiomerically related by a pseudo-mirror plane as shown in Figure 2. This observation is supported by the opposite values of a number of torsional angles as reported in Table 2.

As seen in Figure 2, the P_4C_4 crowns do not directly interact and there are no parallel planar systems in the unit cell. Thus, on the basis of the crystal structure, the deep red colour of (1) is not the result of crystal packing effects. Indeed, the red colour persists in solution confirming that it is a molecular property of (1). On the contrary, complex (2) is yellow. It seems possible to ascribe this colour change to higher conjugative interactions between the phospholyl rings in (1) than in (2).

The P–P bond length in diphosphines and cyclopolyphosphines is known to be remarkably constant at 2.21—2.22 Å [19–21] (except, of course, when cyclic strain is present). Thus, the observed P–P bond lengths in (1) [average 2.191(3) Å] are significantly shorter than a normal P–P single bond. Although these bonds remain much longer than a true isolated P=P double bond (P=P double bond length *ca.* 2.03 Å, see ref. 22), their shortening suggests some fulvalene-like

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* B. Rees, Ph.D. Thesis, University of Strasbourg, 1966. The program was rewritten for a PDP computer by J. F.

conjugation between the two phospholyl moieties of each 1,1′-biphospholyl unit in (1). On the contrary, no such shortening exists in (2) (P–P 2.224 Å).[14] Similarly, the C–C bridges are shorter in (1) [average 1.47(1) Å] than in (2) [1.510(8) Å].[14]

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