

Phosphoryl-Containing Macrocycles. First Examples of [3 + 3] and [4 + 4] Cyclocondensation Compounds Derived from Pyrrole-2,5-dicarboxaldehydes and Phosphodihydrazides

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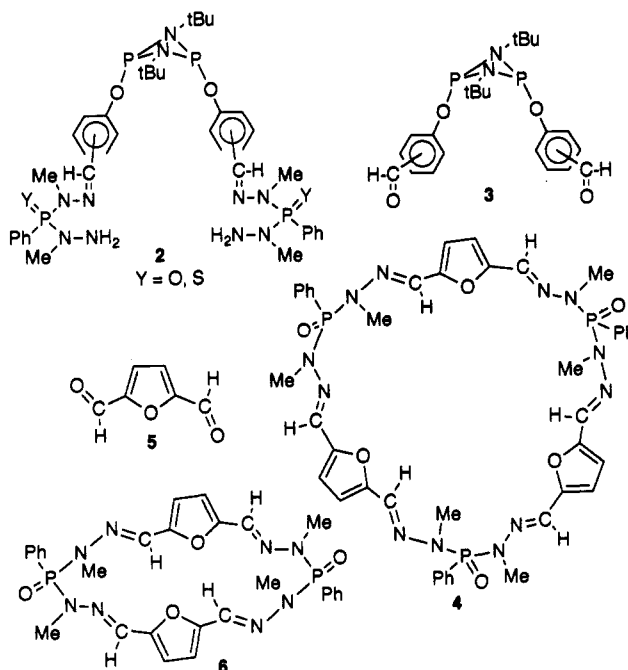
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Due to their propensity to complex a variety of neutral or charged molecules, phosphorus-containing macrocycles have attracted considerable attention during the last decade.¹ Among the numerous ways for synthesizing these macrocyclic species, it can be noted that one of the most useful reactions is the interaction of phosphodihydrazides 1 with dialdehydes: these reactions proceed in very mild conditions, do not necessitate template reactions or high dilution techniques, and remarkably give near-quantitative yields of a number of new macrocycles possessing from one to six phosphorus atoms in the macrocyclic superstructure.²

Two kinds of cyclocondensations were observed. Compounds of the [1 + 1] type were exclusively formed by reacting phosphodihydrazides such as 2 with 1,3 or 1,4 dialdehydes, while a mixture of [1 + 1] and [2 + 2]

macrocycles was obtained when higher dialdehydes, like 3, reacted with phosphodihydrazides 1. Clearly the arm length of the two starting reagents is one of the major factors playing a role in the formation of these macrocycles. Noteworthy, addition of compounds 1 to 1,2, 1,3, 1,4, 1,5, or 1,6 dialdehydes always gave [2 + 2] cyclocondensations. Surprisingly, high-dilution techniques did not dramatically change the course of these reactions. Indeed, only in one case was such a classical technique able to form a [3 + 3] cycloadduct, and even then, compound 4 was obtained in a very poor yield: 1.5%!^{2c}



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(1) Ciampolini, M.; Nardi, N.; Zanobini, F.; Cini, R.; Orioli, P. L. *Inorg. Chim. Acta* 1983, 76, L17. Chivers, T.; Sudhesndra Rao, M. N.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* 1983, 702. Ciampolini, M.; Nardi, N.; Dapporto, P.; Innocenti, P.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* 1984, 575. Ciampolini, M.; Nardi, N.; Orioli, P. L.; Mangani, S.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* 1985, 1425. Brauer, D. J.; Gol, F.; Hietkamp, S.; Peters, H.; Sommer, H.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* 1986, 119, 349. Bradshaw, J. S.; Huszthy, P.; Izatt, R. M. *J. Heterocycl. Chem.* 1986, 23, 1673. Wei, L.; Bell, A.; Warner, S.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* 1986, 108, 8302. Dutasta, J. P. *J. Chem. Res., Synop.* 1986, 22. Lamandé, L.; Munoz, A. *Phosphorus Sulfur* 1987, 30, 459. Von Itzstein, M.; Jenkins, I. D. *J. Chem. Soc., Perkin Trans.* 1987, 2057. Vincens, M.; Gong Cheng, F.; Toulhoat, C.; Grimaldo-Moron, J. T.; Vidal, M. *Tetrahedron Lett.* 1988, 29, 6247. Vincens, M.; Grimaldo-Moron, J. T.; Pasqualini, R.; Vidal, M. *Tetrahedron Lett.* 1987, 28, 1259. Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* 1978, 100, 5567. Tavetkov, E. N.; Bovin, A. N.; Syundyukova V. Kh. *Russ. Chem. Rev.* 1988, 57, 776. Niedermann, H. P.; Eckes, H. L.; Meier, H. *Tetrahedron Lett.* 1989, 30, 155. Widhalm, M. *Monatsh. Chem.* 1990, 121, 1053. Scott, L. T.; Unno, M. *J. Am. Chem. Soc.* 1990, 112, 7823. Wei, L.; Bell, A.; Ahn, K. H.; Holl, M. M.; Warner, S.; Williams, I. D.; Lippard, S. *Inorg. Chem.* 1990, 29, 825. Dutasta, J. P.; Declercq, J. P.; Esteban-Caldoron, C.; Tinant, B. *J. Am. Chem. Soc.* 1989, 111, 7136. Yurchenko, R. I.; Kelpa, T. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* 1990, 60, 2226. Yurchenko, R. I.; Yurchenko, V. G.; Klepa, T. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* 1991, 61, 380. Yurchenko, R. I.; Yurchenko, V. G.; Podgorny, A. V. *Zh. Obshch. Khim.* 1991, 61, 772. Veith, M.; Kross, M.; Labarre, J. F. *J. Mol. Struct.* 1991, 243, 189. Eckes, H. L.; Niedermann, H. P.; Meier, H. *Chem. Ber.* 1991, 124, 377. Talanova, G. G.; Podgorny, A. V.; Zazorina, V. A.; Yatsimirskii, K. B. *Dokl. Akad. Nauk. SSSR.* 1991, 318, 347. Savage, P. B.; Desper, J. M.; Gellman, S. H. *Tetrahedron Lett.* 1992, 33, 2107. Enjalbert, R.; Galy, J.; Galliot, C.; Scheidecker, S.; Bonnet, J. P.; Labarre, J. F. *J. Mol. Struct.* 1992, 271, 95. Dilworth, J. R.; Zheng, Y.; Miller, J. R. *J. Chem. Soc., Dalton Trans.* 1992, 1757. Widhalm, M.; Kratky, C. *Chem. Ber.* 1992, 125, 679. Jones, T. L.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* 1992, 31, 1411. Houalla, D.; Bounja, Z.; Skouta, S. *Tetrahedron Lett.* 1992, 33, 2817.

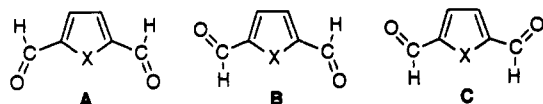
Therefore, the major question to answer is whether it is possible to prepare, in substantial amounts, phosphorus-containing macrocycles arising from [3 + 3] or even [4 + 4] cyclocondensations? To the best of our knowledge, no reactions of these types have been reported so far in phosphorus macrocyclic chemistry. It can be expected that such derivatives might enhance or diversify the possibilities of complexation of cations, anions, or neutral molecules.^{2a,g,h,i}

We report here the preparation, for the first time, of [3 + 3] macrocycles which are obtained in excellent yields (>70%) as well as a single example of [4 + 4] cyclocondensation. Crystal and molecular structure studies of a macrocycle resulting from [2 + 2] cyclocondensation are also described.

(2) (a) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* 1988, 27, 3878. (b) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Gorgues, A.; Delmas, M.; Gaset, A. *Phosphorus Sulfur Silicon* 1990, 49-50, 413. (c) Badri, M.; Majoral, J.-P.; Caminade, A.-M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* 1990, 112, 5618. (d) Badri, M.; Majoral, J.-P.; Goncé, F.; Caminade, A.-M.; Sallé, M.; Gorgues, A. *Tetrahedron Lett.* 1990, 31, 6343. (e) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* 1991, 30, 344. (f) Majoral, J.-P.; Badri, M.; Caminade, A.-M. *Heteroatom Chem.* 1991, 2, 45. (g) Goncé, F.; Caminade, A.-M.; Majoral, J.-P. *Tetrahedron Lett.* 1991, 32, 203. (h) Colombo, D.; Caminade, A.-M.; Majoral, J.-P. *Inorg. Chem.* 1991, 30, 3367. (i) Goncé, F.; Caminade, A.-M.; Boutonnet, F.; Majoral, J.-P. *J. Org. Chem.* 1992, 57, 970. (j) Goncé, F.; Caminade, A.-M.; Majoral, J.-P.; Jaud, J.; Vignaux, J. *Bull. Soc. Chim. Fr.* 1992, 129, 237. (k) Delavaux Nicot, B.; Mathieu, R.; Lugan, N.; Majoral, J.-P. *Inorg. Chem.* 1992, 31, 334. (l) Oussaid, B.; Garrigues, B.; Caminade, A.-M.; Majoral, J.-P. *Phosphorus Sulfur Silicon* 1992, 73, 41.

Results and Discussion

We have already demonstrated that the reaction of furan-2,5-dicarboxaldehyde (5) with phosphodihydrazide 1 led to 20-membered rings such as 6 in near-quantitative yield. An experimental and theoretical study on compound 5, by means of dipole moment analysis and molecular orbital AM₁-calculated enthalpies,³ allowed us to conclude that in solution 5 exists mainly in conformation B (up to 96% in benzene), conformation A being present only in



small amount. On the other hand, it has also been demonstrated by either theoretical calculations,⁴ NMR,⁵ or dipole moment analysis⁶ that pyrrole-2,5-dicarboxaldehyde (7) and the corresponding 1-methylpyrrole-2,5-dicarboxaldehyde (8) were mainly in conformation A [70–85% for 7; 87% for 8⁷]. In all cases, the percentage of form C is small. Such observations prompted us to investigate the reactivity of derivatives 7 and 8 toward phosphodihydrazides 1 in the hope of finding different chemical behaviors for these dialdehydes and therefore different types of cyclocondensations.

Indeed, slow addition of a methanolic solution of the phosphodihydrazide 1a and a methanolic solution of the pyrrole-2,5-dicarboxaldehyde (7) to methanol led to the formation of the 30-membered ring 9'' which precipitated as soon as it was formed (43% yield). Two other compounds were isolated from the mother liquor: the 20-membered ring 9' was obtained in 4% yield, and the 40-membered ring 9''' was obtained in a 4% yield also (Scheme I). These three macrocycles presented different ³¹P chemical shifts: 9', $\delta = 0.92$; 9'', $\delta = 2.78$; and 9''', $\delta = 1.79$ ppm. Structures for these species were deduced from ¹H and ¹³C NMR and IR spectroscopies and elemental analysis and unambiguously by mass spectrometry (fast atom bombardment) which clearly showed the formation of [2 + 2], [3 + 3], and [4 + 4] cyclocondensation products for 9', 9'', and 9''', respectively. Therefore, the use of pyrrole-2,5-dicarboxaldehyde instead of furan-2,5-dicarboxaldehyde dramatically changed the course of the reaction allowing us to obtain, for the first time, a [3 + 3] cyclocondensation derivative in appreciable yield and to isolate the first phosphorus-containing macrocycle arising from a [4 + 4] cyclocondensation reaction. Yield of the 30-membered ring 9'' can be increased from 43 to 74% by using acetonitrile instead of methanol as the solvent of the reaction. Similarly, addition of pyrrole-2,5-dicarboxaldehyde (7) to the phosphodihydrazide 1b gave rise to another [3 + 3] species, the macrocycle 10'' in 74% yield (Scheme I).

Reaction of 1-methylpyrrole-2,5-dicarboxaldehyde (8) with phosphodihydrazide 1a afforded mainly the macro-

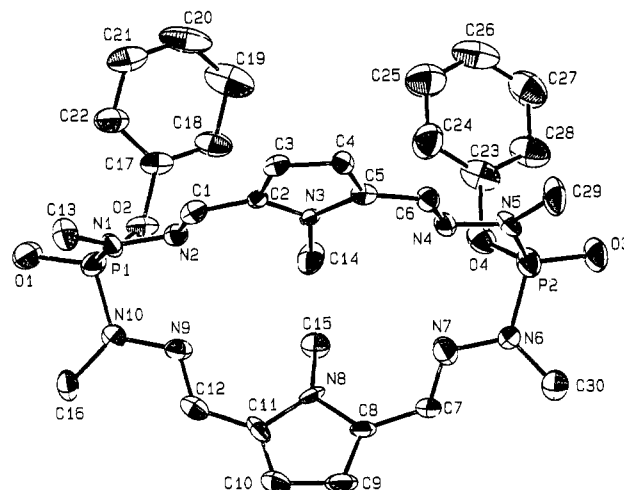
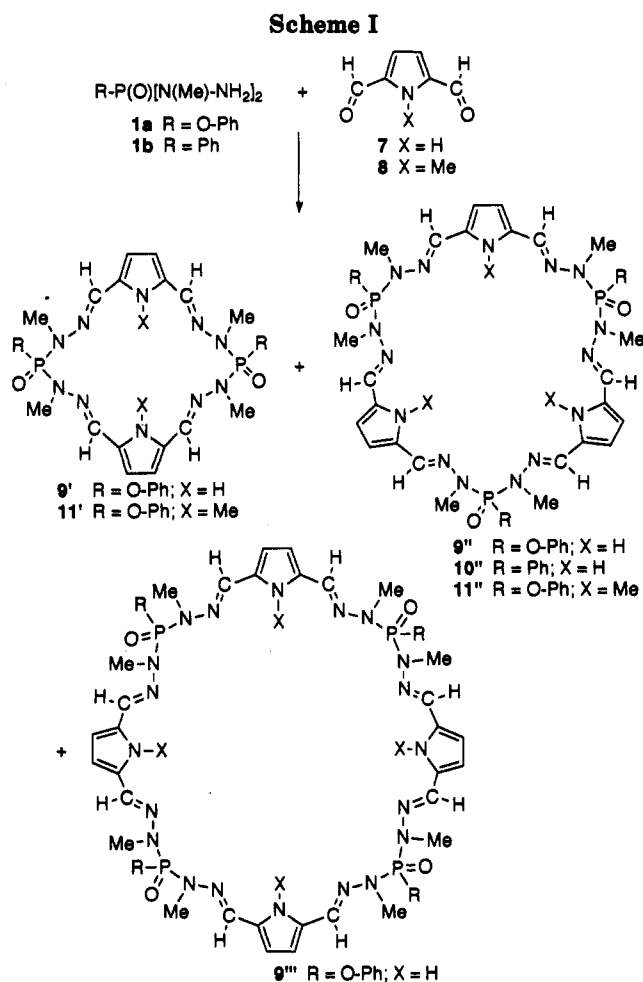


Figure 1.



cycle 11'' (68% yield). This macrocycle, possessing three N–N–P–N–N linkages, was isolated and fully characterized along with the [2 + 2] macrocycle 11' (4% yield). Attempts to isolate the corresponding compound resulting from [4 + 4] cyclocondensation have failed until now. The structure of 11' was confirmed by X-ray crystallography. The ORTEP drawing of this derivative shows the atomic numbering scheme we have used in Figure 1. Selected bond lengths and angles are listed in Table I. Several remarkable features can be pointed out. Although the two phosphorus atoms have the same environment it can be noted that there is a significant difference in the angles

(3) (a) Lumbroso, H.; Curé, J.; Descotes, G.; Grassi, A. *J. Mol. Struct.* 1989, 196, 227 and references cited therein. (b) Hernandez-Fuentes, I.; Abradelo, C.; Dominguez, C.; Csaky, A.; Plumet, J.; Cativiela, C.; Majoral, J.; Gaset, A.; Rigal, L. *Heterocycles* 1989, 29, 657 and references cited therein.

(4) Lumbroso, H.; Pappalardo, G. C. *J. Chim. Phys.* 1974, 71, 3.

(5) Farnier, M.; Drakenberg, T. *J. Chem. Soc., Perkin Trans. 2* 1975, 337.

(6) Bertin, D. M.; Farnier, M.; Liegeois, C. *Bull. Soc. Chim. Fr.* 1974, 2677.

(7) Oussaid, B.; Hubert, C.; Fayet, J.-P.; Garrigues, B. *Bull. Soc. Chim. Fr.*, in press.

Table I. Selected Bond Lengths and Angles for 11'

bond, Å		angle, deg	
P(1)-N(1)	1.657(6)	N(1)-P(1)-N(10)	112.8(6)
P(1)-N(10)	1.643(1)	O(1)-P(1)-N(10)	109.9(5)
P(1)-O(1)	1.437(9)	O(1)-P(1)-N(1)	109.8(5)
P(1)-O(2)	1.583(9)	O(2)-P(1)-N(10)	100.3(5)
P(2)-N(5)	1.648(7)	N(5)-P(2)-N(6)	113.2(6)
P(2)-N(6)	1.656(6)	O(3)-P(2)-N(6)	111.0(6)
P(2)-O(3)	1.449(8)	O(3)-P(2)-N(5)	109.5(5)
P(2)-O(4)	1.569(7)	O(4)-P(2)-N(6)	99.7(5)
N(1)-N(2)	1.40(1)	C(4)-H(41)...O'(3)	166° ^a
N(9)-N(10)	1.40(1)	C(13)-H(133)...O''(3)	171° ^a
N(4)-N(5)	1.39(1)	C(4)...O(3)	3.32 Å
N(6)-N(7)	1.39(1)	H(41)...O(3)	2.35 Å
N(2)-C(1)	1.28(1)	C(13)...O(3)	3.50 Å
N(9)-C(12)	1.29(1)	H(133)...O(3)	2.51 Å
N(4)-C(6)	1.27(1)		
N(7)-C(7)	1.27(1)		

^a Prime position is deduced from the general position by the symmetry [$x - 1/2; y; -z - 1/2$]. Second position is deduced from the general position by the symmetry [$x + 3/2; -y + 1/2; -z$].

around phosphorus: 112°8(6) for N₍₁₎P₍₁₎N₍₁₀₎ and only 99°7(5) for O₍₄₎P₍₂₎N₍₆₎. In comparison, macrocycle 6 exhibited NPN of 104°8(1). Examination of the structure showed that all the atoms, when going from N₍₁₎ to N₍₅₎, are nearly in the same plane defined by N₍₃₎C₍₂₎C₍₃₎C₍₄₎C₍₅₎, while all the atoms, when going from N₍₁₀₎ to N₍₆₎, are in the same plane defined by N₍₈₎C₍₈₎C₍₉₎C₍₁₀₎C₍₁₁₎. It is noteworthy that these two planes are nearly orthogonal (93°5).

This is a very compact macrocycle made even more so by the orientation of the phenyl groups participating in the closure of the molecule. Analysis of the structure with the help of a Platon program⁸ show that there is no hole in this structure! Moreover, the cohesion of this molecule is reinforced by the existence of intermolecular hydrogen bonding between the C₍₄₎H₍₄₁₎O'(3) system and the C₍₁₃₎H₍₁₃₃₎O''(3) system (see Table I). Attention can also be focused on the fact that the N=C-pyrrole-C=N parts of this macrocycle adopted the *same* conformation of that of the starting 1-methylpyrrole-2,5-dicarboxaldehyde (8), i.e., conformation A. This can be related to the observation that the conformation of N=C-furan-C=N part of the macrocycle 6 is also the same for that of the starting furan-2,5-dicarboxaldehyde (conformation B). Therefore, it seems that the structure of the dialdehyde partly induced the geometry of the resulting macrocycle. This conclusion has to be confirmed, of course, by other experiments, but it seems of high importance for the prediction of the conformation of these phosphorus-containing macrocycles. Nevertheless, one question does remain unresolved: why did conformation A induce mainly [3 + 3] cyclocondensations while conformation B led near-quantitatively to compounds of the [2 + 2] type? Work is in progress to try to answer this question and to study the reactivity of all these new macrocyclic species.

Experimental Section

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ¹H and ¹³C NMR spectra were recorded on Bruker AC 80 and AC 200 spectrometers. ³¹P NMR chemical shifts are reported in ppm relative to 85% H₃-PO₄. Mass spectra were obtained by methane desorption or fast atom bombardment. Silica gel columns were used for purification of macrocycles. The literature procedures were employed for

the synthesis of the known phosphodihydrazides 1a and 1b⁹ and the pyrrole-2,5-dicarboxaldehyde 7¹⁰ and 8.¹¹ Due to space consumption, only a few representative systematic names are given.¹²

Synthesis of macrocycles 9', 9'', and 9'''. A solution of phosphodihydrazide 1a (0.01 mol, 2.30 g) in 30 mL of methanol and a solution of pyrrole-2,5-dicarboxaldehyde (7) (0.01 mol, 1.23 g) in 30 mL of methanol were simultaneously and slowly added to 10 mL of methanol. The resulting mixture was stirred for 1 week during which time a precipitate was formed. This precipitate, which corresponds to the macrocycle 9'', is purified by column chromatography (eluent: methanol/chloroform (1/9), *R_f* 0.36). After evaporation of the filtrate and purification by column chromatography the two macrocycles 9' (eluent: ethyl acetate, *R_f* 0.58) and 9''' (eluent: ethyl acetate, *R_f* 0.48) were isolated.

9': yield 4%; mp 119 °C; ³¹P{¹H} NMR (CDCl₃) δ 0.92 (s); ¹H NMR (CDCl₃) δ 12.60 (s, 2H, NH), 7.42 (d, 4H, ³J_{HP} = 2.3 Hz, HC=N), 7.33 (m, 10H, arom), 6.22 (d, 4H, ⁴J_{HNH} = 2.3 Hz, HCC), 3.17 (d, 12H, ³J_{HP} = 8.3 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃) δ 150.1 (d, ²J_{CP} = 6.6 Hz, C ipso), 131.3 (s, C₂ and C₅ pyr), 131.0 (d, ³J_{CP} = 15.5 Hz, C=N), 130.0 (s, arom), 125.4 (s, arom), 120.7 (d, ²J_{CP} = 4.5 Hz arom), 112.1 (s, C₃ and C₄ pyr), 31.8 (d, ²J_{CP} = 8.4 Hz, CH₃); IR (KBr) 3186 (ν_{NH}), 1651 (ν_{C=N}), 1270 (ν_{P=O}) cm⁻¹; MS 635 [M + 1]⁺. Anal. Calcd for C₂₈H₃₂N₁₀O₄P₂: C, 53.00; H, 5.08; N, 22.07. Found: C, 52.44; H, 4.98; N, 21.68.

9'': yield 43%; mp 236 °C; ³¹P{¹H} NMR (CDCl₃) δ 2.78 (s); ¹H NMR (CDCl₃) δ 10.05 (br s, 3H, NH), 7.43 (s, 6H, HC=N), 7.42-7.10 (m, 15H, arom), 6.27 (s, 6H, HCC), 3.18 (d, ³J_{HP} = 7.5 Hz, 18H, CH₃); ¹³C{¹H} NMR (CDCl₃) δ 150.2 (s, C ipso), 130.6 (s, C₂ and C₅ pyr), 129.8 (s, C=N), 129.4 (s, arom), 125.2 (s, arom), 120.6 (s, arom), 112.0 (s, C₃ and C₄ pyr), 32.6 (s, CH₃); IR (KBr) 3160 (ν_{NH}), 1637 (ν_{C=N}), 1269 (ν_{P=O}) cm⁻¹; MS 952 [M + 1]⁺. Anal. Calcd for C₄₂H₄₈N₁₅O₆P₃: C, 53.00; H, 5.08; N, 22.07. Found: C, 52.14; H, 4.96; N, 21.60.

9''': yield 4%; mp 245 °C; ³¹P{¹H} NMR (CDCl₃) δ 1.79 (s); ¹H NMR (CDCl₃) δ 12.3 (s, 4H, NH), 7.42 (s, 8H, HC=N), 7.31-7.11 (m, 20H, arom), 6.26 (s, 8H, HCC), 3.17 (d, 24H, ³J_{HP} = 7.5 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃) δ 150.2 (d, ²J_{CP} = 6.6 Hz, C ipso), 131.3 (s, C₂ and C₅ pyr), 131.2 (d, ³J_{CP} = 14.7 Hz, C=N), 129.8 (s, arom), 125.3 (s, arom), 121.1 (d, ²J_{CP} = 4.5 Hz, arom), 113.1 (s, C₃ and C₄ pyr), 31.6 (d, ²J_{CP} = 10.5 Hz, CH₃); IR (KBr) 3186 (ν_{NH}), 1651 (ν_{C=N}), 1267 (ν_{P=O}) cm⁻¹; MS 1269 [M + 1]⁺. Anal. Calcd for C₆₆H₈₄N₂₀O₈P₄: C, 53.00; H, 5.08; N, 22.07. Found: C, 52.71; H, 4.85; N, 21.87.

Synthesis of Macrocycles 11' and 11''. A solution of phosphodihydrazide 1a (0.01 mol, 2.30 g) in 30 mL of acetonitrile and a solution of 1-methylpyrrole-2,5-dicarboxaldehyde (8) (0.01 mol, 1.37 g) in 30 mL of acetonitrile was simultaneously added to 20 mL of acetonitrile. The resulting mixture was stirred for 1 week, during which time a precipitate was formed. This precipitate, macrocycle 11'', was purified by column chromatography (eluent: methanol/chloroform (1/9), *R_f* 0.40). Evaporation of the filtrate and purification by column chromatography allowed us to isolate some additional compound 11' and the 20-membered ring 11' (eluent: ethyl acetate, *R_f* 0.48).

11': yield 4%; mp 218 °C; ³¹P{¹H} NMR (CDCl₃) δ 0.19 (s); ¹H NMR (CDCl₃) δ 7.41-7.08 (m, 14H, arom and HC=N), 6.18 (s, 4H, HCC), 4.23 (s, 6H, CH₃NC), 3.25 (d, ³J_{HP} = 8.1 Hz, 12H, CH₃NN); ¹³C{¹H} NMR (CDCl₃) δ 151.2 (d, ²J_{CP} = 6.5 Hz, C ipso), 133.0 (s, C₂ and C₅ pyr), 131.9 (d, ³J_{CP} = 15.1 Hz, C=N), 129.5 (s, arom), 124.6 (s, arom), 119.7 (d, ²J_{CP} = 5.9 Hz, arom), 114.35 (s, C₃ and C₄ pyr), 36.8 (s, CH₃NC), 31.1 (d, ²J_{CP} = 10.6 Hz, CH₃NN); IR (KBr) 1660 (ν_{C=N}), 1269 (ν_{P=O}) cm⁻¹; MS 663 [M + 1]⁺. Anal. Calcd for C₃₀H₃₆N₁₀O₄P₂·0.5CH₃CO₂C₂H₅: C, 54.39; H, 5.70; N, 19.82. Found: C, 54.20; H, 5.33; N, 20.00.

(9) Majoral, J.-P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* 1976, 32, 2633.

(10) Miller, R.; Olosson, K. *Acta. Chem. Scand. B* 1981, 35, 303.

(11) Cresp, T. M.; Sargeni, M. V. *J. Chem. Soc., Chem. Commun.* 1972, 807. Severin, T.; Ipachi, I. *Chem. Ber.* 1975, 108, 1768.

(12) Some representative names: 9', 4,6,15,17-tetramethyl-5,16 diphenox-23,24-diaza-3,4,6,7,14,15,17,18-octaaza-5,16-diphosphatricyclo[18.2.1.1^{9,12}]tetracos-2,7,9,11,13,18,20,22-octaene 5,16 dioxide; 9'', 4,6,15,17,26,28-hexamethyl-5,16,27-triphenox-34,35,36-triaza-3,4,6,7,14,15,17,18,25,26,28,29-dodecaaza-5,16,27-triphosphatetracyclo[29.2.1.1^{9,12}.1^{20,23}]hexatriaconta-2,7,9,11,13,18,20,22,24,29,31,33-dodecaene 5,16,27-trioxide.

(8) Le Page, Y. *J. Appl. Crystallogr.* 1987, 20, 264; *J. Appl. Crystallogr.* 1988, 21, 983.

11'': yield 68%; mp 175 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 2.53 (s); ^1H NMR (CDCl_3) δ 7.47 (s, 6H, HC=N), 7.25–7.20 (m, 15H, arom), 6.29 (s, 6H, HC-C), 3.97 (s, 9H, CH_3NC), 3.18 (d, $^3J_{\text{HP}} = 7.5$ Hz, 18H, CH_3NN); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 150.4 (s, C ipso), 131.9 (s, C₂ and C₅ pyr), 131.4 (s, C=N), 129.7 (s, arom), 125.0 (s, arom), 120.5 (s, arom), 113.3 (s, C₃ and C₄ pyr), 34.8 (s, $\text{CH}_3\text{-NC}$), 31.9 (s, CH_3NP); IR (KBr) 1660 ($\nu_{\text{C-N}}$), 1267 ($\nu_{\text{P-O}}$) cm^{-1} ; MS 994 [$\text{M} + 1$]⁺. Anal. Calcd for $\text{C}_{45}\text{H}_{54}\text{N}_{15}\text{O}_6\text{P}_3$: C, 54.37; H, 5.48; N, 21.14. Found: C, 53.87; H, 5.11; N, 20.75.

Macrocyclic 10'' was prepared following the same procedure as for derivatives 9'' and 11'' and was purified on column chromatography (eluent: methanol/chloroform (1/9), R_f 0.42). 10'': yield 74%; mp 219 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 23.57 (s); ^1H NMR (CDCl_3) δ 9.50 (br s, 3H, NH), 7.8–7.34 (m, 21H, HC=N, arom), 6.22 (s, 6H, HCC), 3.02 (d, $^3J_{\text{HP}} = 8.2$ Hz, 18H, CH_3NP); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 132.3 (d, $^3J_{\text{CP}} = 16.2$ Hz, C=N), 131.0 (s, arom), 130.6 (s, C=CNH), 129.7 (s, arom), 129.0 (d, $^1J_{\text{CP}} = 157$ Hz, CP), 128.3 (d, $J_{\text{CP}} = 14.1$ Hz, arom), 112.0 (s, CCNH) 31.4 (br s, $\text{H}_3\text{-CNP}$); IR (KBr) 3232 (ν_{NH}), 1636 ($\nu_{\text{C-N}}$), 1236 ($\nu_{\text{P-O}}$) cm^{-1} ; MS 904 [$\text{M} + 1$]⁺. Anal. Calcd for $\text{C}_{42}\text{H}_{46}\text{N}_{16}\text{O}_3\text{P}_3$: C, 55.81; H, 5.35; N, 23.24. Found: C, 55.80; H, 5.53; N, 22.90.

Crystal data for 11' are given in Table II. Unit cell parameters, space group, and data collection were obtained on an Enraf-Nonius CAD 4 automatic diffractometer. The intensity of three standard reflections [(230) (041) (213)] were monitored every hour. They showed no variation during data collection. Corrections were made for Lorentz and polarization effects. ψ scan curves around diffusion vectors showed no significant intensity variation, and thus no absorption corrections were applied.

Computations were performed using the CRYSTALS system from Oxford University adapted on a mini super calculator Alliant VF X 80. Most atoms were localized by direct methods (Shelxs 86). All remaining non-hydrogen atoms were found by structure factor and Fourier series calculations. All non-hydrogen atoms

Table II. Crystal Data and Summary of Structure Determination of 11'

formula	$\text{C}_{30}\text{H}_{36}\text{N}_{10}\text{O}_4\text{P}_2$
mol. wt (g)	662
crystal system	orthorhombic
space group, Z	$Pbca$, 8
a (Å)	14.156(6)
b (Å)	17.089(5)
c (Å)	26.953(5)
V (Å ³)	6520(4)
d (calcd) (g cm^{-3})	1.35
$F(000)$	2784
μ (Mo $K\alpha$) (cm^{-1})	1.8
crystal size (mm^3)	$0.2 \times 0.3 \times 0.5$
take off (deg)	4.2
detector width (mm)	4×4
scan width (deg)	$0.7 + 0.347 \text{tg } \theta$
θ range (deg)	27
no. of meas reflns	5650
no. of variables	415
no. of unique reflns with $I > 3\sigma$	1568
weighting scheme, W	1
agreement factors R	0.060
R_w	0.060

were refined with anisotropic thermal parameters. Hydrogen atoms were located by difference Fourier techniques, and then all the hydrogen atoms were fixed at 1 Å from their carbon atoms. They were not further refined in the final stages of calculation. No important residue remained in the final difference map.

The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.