Table S1. Crystal data and structure refinement for $C_{12}H_{42}N_6O_{16}P_4$.

Empirical formula	$C_{12}H_{42}N_6O_{16}P_4$
Formula weight	650.4
Temperature	298 K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	*P 2₁/n*
Unit cell dimensions	*a* = 9.201(8) Å alpha = 90 deg.
	b = 12.617(7) Å beta = 104.59(6) deg.
	c = 11.838(9) Å gamma = 90 deg.
Volume	1330(2) $Å^3$
Z	2
Density (calculated)	1.624 Mg/m^3
Absorption coefficient	0.367 mm^{-1}
F(000)	688
Crystal size	0.07 x 0.25 x 0.3 mm
Theta range for data collection	2.52 to 24.97 deg.
Index ranges	$-10 \le h \le 10$, $0 \le k \le 14$, $0 \le l \le 14$
Scan rate	variable
Scan mode	θ - 2θ
Scan width	0.9 + 0.35 tg θ
Reflections collected	2046
Independent reflections	1963
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1960 / 0 / 187
Goodness-of-fit on F^2	0.996
Unique obs. reflections [$I>2\sigma(I)$]	1336
Transmission factors	0.90 - 0.97
w	$1 / [\sigma^2(F_o^2) + (0.1786\ P)^2]^{½}$
P	$F_o^2 / 3 + 2\ F_c^2 / 3$
Final R indices [$I>2\sigma(I)$]	R1 = 0.1010, wR2 = 0.2452*
R indices (all data)	R1 = 0.1428, wR2 = 0.2698*
Largest diff. peak and hole	0.552 and -1.140 $e.Å^{-3}$

* $R1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$; $wR2 = [\Sigma\ w(F_o^2 - F_c^2)^2 / \Sigma\ wF_o^4]^{½}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $C_{12}H_{40}N_6O_{16}P_4$.

	x/a	y/b	z/c	U(eq)
P(1)	-2755(2)	1255(2)	-365(2)	25(1)
O(1)	-1984(7)	2149(5)	-792(5)	38(2)
O(2)	-1804(8)	317(5)	-8(6)	48(2)
O(3)	-3414(8)	1725(6)	630(6)	49(2)
O(4)	-4246(6)	932(5)	-1344(5)	32(2)
P(2)	-4505(2)	-74(2)	-2201(2)	26(1)
O(5)	-3323(7)	-61(5)	-2873(5)	35(2)
O(6)	-4561(8)	-1038(5)	-1495(6)	43(2)
O(7)	-6086(7)	153(5)	-2998(5)	39(2)
O(8)	1529(12)	-4090(6)	12(6)	76(3)
C(1)	187(11)	828(8)	-3268(8)	40(2)
N(1)	-412(12)	-1534(9)	2279(9)	43(3)
C(2)	-1929(14)	-1789(11)	1747(10)	36(3)
N(1')	-1405(38)	-1074(28)	2025(29)	24(7)
C(2')	-1321(49)	-2290(36)	1800(35)	26(9)
C(3)	-2020(11)	-2409(7)	618(8)	36(2)
N(2)	-1161(8)	-1821(6)	-115(7)	27(2)
C(4)	-1456(10)	-2236(7)	-1331(8)	33(2)
C(5)	-377(11)	-1836(8)	-2001(8)	37(2)
N(3)	-403(10)	-676(6)	-2139(7)	29(2)
C(6)	402(11)	-321(8)	-3023(8)	39(2)

Table S3. Bond lengths [Å] and angles [deg] for $C_{12}H_{40}N_6O_{16}P_4$.

P(1)-O(2)	1.470(7)
P(1)-O(1)	1.487(7)
P(1)-O(3)	1.570(7)
P(1)-O(4)	1.609(6)
O(4)-P(2)	1.604(6)
P(2)-O(6)	1.484(7)
P(2)-O(5)	1.500(6)
P(2)-O(7)	1.547(6)
C(1)-N(1)#1	1.444(14)
C(1)-C(6)	1.482(14)
C(1)-N(1')#1	1.64(3)
N(1)-N(1')	1.06(3)
N(1)-C(2')	1.30(4)
N(1)-C(2)	1.42(2)
N(1)-C(1)#1	1.444(14)
C(2)-C(2')	0.84(4)
C(2)-N(1')	1.04(3)
C(2)-C(3)	1.53(2)
N(1')-C(2')	1.56(5)
N(1')-C(1)#1	1.64(3)
C(2')-C(3)	1.39(4)
C(3)-N(2)	1.507(12)
N(2)-C(4)	1.492(11)
C(4)-C(5)	1.505(14)
C(5)-N(3)	1.473(12)
N(3)-C(6)	1.495(12)

O(2)-P(1)-O(1)	114.1(4)
O(2)-P(1)-O(3)	113.7(4)
O(1)-P(1)-O(3)	106.0(4)
O(2)-P(1)-O(4)	109.9(3)
O(1)-P(1)-O(4)	109.9(4)
O(3)-P(1)-O(4)	102.5(4)
P(2)-O(4)-P(1)	128.3(4)
O(6)-P(2)-O(5)	116.1(4)
O(6)-P(2)-O(7)	109.5(4)
O(5)-P(2)-O(7)	111.7(4)
O(6)-P(2)-O(4)	108.2(4)
O(5)-P(2)-O(4)	108.3(3)
O(7)-P(2)-O(4)	101.9(3)
N(1)#1-C(1)-C(6)	117.4(9)
N(1)#1-C(1)-N(1')#1	39.6(12)
C(6)-C(1)-N(1')#1	89.0(14)
N(1')-N(1)-C(2')	82(3)
N(1')-N(1)-C(2)	47(2)
C(2')-N(1)-C(2)	36(2)
N(1')-N(1)-C(1)#1	80(2)
C(2')-N(1)-C(1)#1	139(2)
C(2)-N(1)-C(1)#1	115.1(10)
C(2')-C(2)-N(1')	113(4)
C(2')-C(2)-N(1)	65(3)

N(1')-C(2)-N(1)	48(2)
C(2')-C(2)-C(3)	64(3)
N(1')-C(2)-C(3)	130(2)
N(1)-C(2)-C(3)	109.6(10)
C(2)-N(1')-N(1)	85(3)
C(2)-N(1')-C(2')	30(2)
N(1)-N(1')-C(2')	56(2)
C(2)-N(1')-C(1)#1	127(3)
N(1)-N(1')-C(1)#1	60(2)
C(2')-N(1')-C(1)#1	107(3)
C(2)-C(2')-N(1)	80(4)
C(2)-C(2')-C(3)	83(3)
N(1)-C(2')-C(3)	127(3)
C(2)-C(2')-N(1')	38(3)
N(1)-C(2')-N(1')	42(2)
C(3)-C(2')-N(1')	104(3)
C(2')-C(3)-N(2)	110(2)
C(2')-C(3)-C(2)	33(2)
N(2)-C(3)-C(2)	109.2(8)
C(3)-N(2)-C(4)	112.9(7)
N(2)-C(4)-C(5)	114.0(7)
N(3)-C(5)-C(4)	113.4(8)
C(5)-N(3)-C(6)	112.2(8)
C(1)-C(6)-N(3)	111.3(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $C_{12}H_{40}N_6O_{16}P_4$.

	U11	U22	U33	U23	U13	U12
P(1)	29(1)	20(1)	25(1)	-1(1)	4(1)	1(1)
O(1)	37(3)	38(4)	37(4)	7(3)	7(3)	-2(3)
O(2)	49(4)	33(4)	45(4)	-2(3)	-20(3)	9(3)
O(3)	59(5)	52(4)	43(4)	-32(3)	24(3)	-24(4)
O(4)	27(3)	29(3)	37(3)	-5(3)	2(3)	6(3)
P(2)	28(1)	26(1)	25(1)	-1(1)	9(1)	-1(1)
O(5)	30(3)	39(4)	37(3)	-8(3)	9(3)	3(3)
O(6)	51(4)	37(4)	53(4)	11(3)	33(4)	9(3)
O(7)	25(3)	50(4)	37(3)	-6(3)	2(3)	-4(3)
O(8)	142(9)	48(5)	30(4)	-2(3)	5(5)	-39(5)
C(1)	39(5)	41(6)	37(5)	4(5)	6(4)	-2(5)
C(3)	39(5)	23(5)	46(6)	6(4)	11(4)	-6(4)
N(2)	26(4)	15(4)	42(4)	-5(3)	9(3)	-2(3)
C(4)	29(5)	24(5)	41(5)	-17(4)	1(4)	-9(4)
C(5)	36(5)	36(6)	34(5)	-18(4)	4(4)	1(4)
N(3)	33(4)	26(4)	30(4)	-9(3)	10(4)	0(4)
C(6)	47(6)	40(6)	36(5)	2(4)	22(5)	-3(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $C_{12}H_{40}N_6O_{16}P_4$.

	x/a	y/b	z/c	U(eq)
H(1A)	-823	1062	-3317	54(10)
H(1B)	499	1035	-3965	54(10)
H(1C)	885	1038	-3723	54(10)
H(1D)	-812	939	-3739	54(10)
H(2C)	-2483	-1152	1600	54(10)
H(2D)	-2280	-2224	2294	54(10)
H(2'C)	-779	-2353	2312	54(10)
H(2'D)	-2483	-2157	2193	54(10)
H(3A)	-3084	-2361	284	54(10)
H(3B)	-1742	-3162	657	54(10)
H(3C)	-1619	-3114	789	54(10)
H(3D)	-3071	-2464	202	54(10)
H(2A)	-45(140)	-1825(93)	339(96)	55(35)
H(2B)	-1470(82)	-1187(69)	-165(62)	14(20)
H(4A)	-2468(10)	-2040(7)	-1750(8)	54(10)
H(4B)	-1406(10)	-3004(7)	-1302(8)	54(10)
H(5A)	632(11)	-2054(8)	-1599(8)	54(10)
H(5B)	-620(11)	-2162(8)	-2767(8)	54(10)
H(3A)	102(72)	-318(53)	-1378(57)	1(16)
H(3B)	-1162(121)	-401(88)	-2249(93)	27(37)
H(6A)	1467	-433	-2733	54(10)
H(6B)	42	-689	-3738	54(10)
H(6C)	1463	-470	-3738	54(10)
H(6D)	28	-708	-3738	54(10)

Table S6. Weighted least-squares planes through the starred atoms for $C_{12}H_{40}N_6O_{16}P_4$ (Nardelli, Musatti, Domiano & Andreetti Ric.Sci.(1965),15(II-A),807).
Equation of the plane: m1*X+m2*Y+m3*Z=d

Plane 1
m1 = -0.91352(0.00072)
m2 = 0.36931(0.00184)
m3 = -0.17057(0.00196)
D = 0.00000(0.00395)

Atom	d	s	d/s	(d/s)**2
N1 *	-0.1932	0.0111	-17.485	305.718
N2 *	0.1190	0.0080	14.840	220.225
N3 *	-0.1410	0.0090	-15.622	244.040
N1S *	0.1932	0.0111	17.485	305.718
N2S *	-0.1190	0.0080	-14.840	220.225
N3S *	0.1410	0.0090	15.622	244.040

Table S7. Crystal data and structure refinement for $C_{14}H_{54}N_6O_{20}P_4$.

Empirical formula	$C_{14}H_{54}N_6O_{20}P_4$
Formula weight	750.51
Temperature	298 K
Wavelength	1.54178 Å
Crystal system	triclinic
Space group	P $\bar{1}$
Unit cell dimensions	*a* = 11.009(2) Å alpha = 110.71(2) deg.
	b = 13.286(2) Å beta = 112.830(10) deg.
	c = 13.450(2) Å gamma = 90.820(10) deg.
Volume	1669.6(5) $Å^3$
Z	2
Density (calculated)	1.493 Mg/m^3
Absorption coefficient	2.867 mm^{-1}
F(000)	800
Crystal size	0.2 x 0.15 x 0.1 mm
Theta range for data collection	3.61 to 59.95 deg.
Index ranges	$0 \le h \le 12, -14 \le k \le 14, -15 \le l \le 13$
Scan rate	variable
Scan mode	θ - 2θ
Scan width	0.9 + 0.20 tg θ
Reflections collected	4863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4861 / 0 / 450
Goodness-of-fit on F^2	1.055
Unique obs. reflections [$I>2\sigma(I)$]	4315
Transmission factors	0.60 - 0.75
w	$1 / [\sigma^2(F_o^2) + (0.1416\ P)^2 + 2.06\ P]^{1/2}$
P	$F_o^2 / 3 + 2\ F_c^2 / 3$
Final R indices [$I>2\sigma(I)$]	R1 = 0.0670, wR2 = 0.1907*
R indices (all data)	R1 = 0.0731, wR2 = 0.1990*
Largest diff. peak and hole	0.703 and -0.970 $e.Å^{-3}$

* $R1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$; $wR2 = [\Sigma\ w(F_o^2 - F_c^2)^2 / \Sigma\ wF_o^4]^{1/2}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $C_{14}H_{54}N_6O_{20}P_4$.

	x/a	y/b	z/c	U(eq)
O(15)	4440(4)	441(3)	7481(3)	60(1)
O(16)	229(4)	3213(3)	4748(3)	67(1)
O(17)	10454(4)	4884(4)	6710(3)	71(1)
O(18)	220(13)	1819(11)	5889(12)	104(4)
O(18')	1188(29)	2041(14)	6142(16)	136(10)
O(19)	3671(5)	-10046(4)	-5748(4)	77(1)
O(20)	2018(7)	-9931(6)	-4676(6)	118(2)
P(1)	4720(1)	2994(1)	-112(1)	29(1)
O(1)	3968(3)	2186(2)	72(3)	38(1)
O(2)	5368(3)	2420(2)	-963(3)	39(1)
O(3)	5769(3)	3875(2)	944(3)	40(1)
O(4)	3652(3)	3564(3)	-842(3)	39(1)
P(2)	2342(1)	3945(1)	-667(1)	32(1)
O(5)	2235(3)	4937(2)	-1046(3)	43(1)
O(6)	2631(3)	4289(3)	599(3)	46(1)
O(7)	1169(3)	3064(3)	-1529(3)	44(1)
P(3)	2942(1)	1383(1)	1922(1)	27(1)
O(8)	2510(3)	2325(2)	2804(2)	30(1)
O(9)	1743(3)	909(2)	761(2)	32(1)
P(4)	2355(1)	3554(1)	2885(1)	29(1)
O(10)	3422(3)	609(2)	2490(3)	39(1)
O(11)	4124(3)	2003(3)	1886(3)	40(1)
O(12)	3726(3)	4243(2)	3491(2)	36(1)
O(13)	1492(3)	3902(3)	3511(3)	41(1)
O(14)	1622(3)	3412(3)	1580(3)	41(1)
N(1)	-1826(3)	985(3)	1482(3)	33(1)
C(13)	-3293(5)	741(4)	871(4)	48(1)
C(1)	-1340(5)	778(4)	2546(4)	40(1)
C(2)	-1538(5)	-433(4)	2278(4)	40(1)
N(2)	-991(4)	-1064(3)	1438(3)	32(1)
C(3)	485(4)	-748(4)	1884(4)	37(1)
C(4)	1056(4)	-1563(4)	1154(4)	36(1)
N(3)	858(4)	-1438(3)	53(3)	31(1)
C(11)	-1458(5)	2261(3)	627(4)	39(1)
C(12)	-1292(5)	2097(3)	1722(4)	40(1)
C(5)	6785(5)	2908(4)	4467(4)	39(1)
C(6)	6085(5)	2425(4)	4998(4)	43(1)
N(4)	6246(4)	3183(3)	6147(3)	41(1)
C(14)	7594(6)	3358(5)	7019(5)	63(2)
C(7)	5229(6)	2796(4)	6462(5)	49(1)
C(8)	5074(6)	3668(4)	7442(4)	48(1)
N(5)	4797(4)	4683(3)	7221(3)	35(1)
C(9)	3461(5)	4553(4)	6279(4)	44(1)
C(10)	3075(5)	5627(4)	6224(4)	42(1)
N(6)	3682(4)	6060(3)	5615(3)	32(1)

Table S9. Bond lengths [Å] and angles [deg] for $C_{14}H_{54}N_6O_{20}P_4$.

P(1)-O(1)	1.492(3)
P(1)-O(3)	1.494(3)
P(1)-O(2)	1.559(3)
P(1)-O(4)	1.605(3)
O(4)-P(2)	1.610(3)
P(2)-O(7)	1.489(3)
P(2)-O(6)	1.495(3)
P(2)-O(5)	1.563(3)
P(3)-O(10)	1.476(3)
P(3)-O(9)	1.503(3)
P(3)-O(11)	1.555(3)
P(3)-O(8)	1.614(3)
O(8)-P(4)	1.613(3)
P(4)-O(13)	1.478(3)
P(4)-O(12)	1.503(3)
P(4)-O(14)	1.559(3)
N(1)-C(1)	1.447(6)
N(1)-C(12)	1.459(5)
N(1)-C(13)	1.469(6)
C(13)-H(13A)	0.96
C(13)-H(13B)	0.96
C(13)-H(13C)	0.96
C(1)-C(2)	1.512(6)
C(1)-H(1A)	0.97
C(1)-H(1B)	0.97
C(2)-N(2)	1.489(5)
C(2)-H(2A)	0.97
C(2)-H(2B)	0.97
N(2)-C(3)	1.490(5)
C(3)-C(4)	1.511(6)
C(3)-H(3A)	0.97
C(3)-H(3B)	0.97
C(4)-N(3)	1.480(5)
C(4)-H(4A)	0.97
C(4)-H(4B)	0.97
N(3)-C(11)#1	1.501(5)
C(11)-N(3)#1	1.501(5)
C(11)-C(12)	1.505(6)
C(11)-H(11A)	0.97
C(11)-H(11B)	0.97
C(12)-H(12A)	0.97
C(12)-H(12B)	0.97
C(5)-N(6)#2	1.496(5)
C(5)-C(6)	1.500(7)
C(5)-H(5A)	0.97
C(5)-H(5B)	0.97
C(6)-N(4)	1.455(6)
C(6)-H(6A)	0.97
C(6)-H(6B)	0.97
N(4)-C(14)	1.441(7)
N(4)-C(7)	1.485(6)
C(14)-H(14A)	0.96

C(14)-H(14B)	0.96
C(14)-H(14C)	0.96
C(7)-C(8)	1.486(7)
C(7)-H(7A)	0.97
C(7)-H(7B)	0.97
C(8)-N(5)	1.492(6)
C(8)-H(8A)	0.97
C(8)-H(8B)	0.97
N(5)-C(9)	1.480(6)
C(9)-C(10)	1.514(7)
C(9)-H(9A)	0.97
C(9)-H(9B)	0.97
C(10)-N(6)	1.482(6)
C(10)-H(10A)	0.97
C(10)-H(10B)	0.97
N(6)-C(5)#2	1.496(5)

O(1)-P(1)-O(3)	118.0(2)
O(1)-P(1)-O(2)	111.6(2)
O(3)-P(1)-O(2)	107.9(2)
O(1)-P(1)-O(4)	107.8(2)
O(3)-P(1)-O(4)	108.1(2)
O(2)-P(1)-O(4)	102.1(2)
P(1)-O(4)-P(2)	126.7(2)
O(7)-P(2)-O(6)	117.2(2)
O(7)-P(2)-O(5)	109.0(2)
O(6)-P(2)-O(5)	112.1(2)
O(7)-P(2)-O(4)	108.4(2)
O(6)-P(2)-O(4)	108.4(2)
O(5)-P(2)-O(4)	100.3(2)
O(10)-P(3)-O(9)	115.2(2)
O(10)-P(3)-O(11)	110.4(2)
O(9)-P(3)-O(11)	113.4(2)
O(10)-P(3)-O(8)	106.0(2)
O(9)-P(3)-O(8)	107.2(2)
O(11)-P(3)-O(8)	103.7(2)
P(4)-O(8)-P(3)	128.9(2)
O(13)-P(4)-O(12)	114.5(2)
O(13)-P(4)-O(14)	111.3(2)
O(12)-P(4)-O(14)	112.6(2)
O(13)-P(4)-O(8)	105.2(2)
O(12)-P(4)-O(8)	108.7(2)
O(14)-P(4)-O(8)	103.7(2)
P(3)-O(11)-H(11)	121(4)
P(4)-O(14)-H(14)	123(4)
C(1)-N(1)-C(12)	110.8(3)
C(1)-N(1)-C(13)	112.2(4)
C(12)-N(1)-C(13)	111.9(4)
N(1)-C(13)-H(13A)	109.5(2)
N(1)-C(13)-H(13B)	109.5(2)
H(13A)-C(13)-H(13B)	109.5
N(1)-C(13)-H(13C)	109.4(2)
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

N(1)-C(1)-C(2)	111.3(3)
N(1)-C(1)-H(1A)	109.4(2)
C(2)-C(1)-H(1A)	109.4(2)
N(1)-C(1)-H(1B)	109.4(2)
C(2)-C(1)-H(1B)	109.4(3)
H(1A)-C(1)-H(1B)	108.0
N(2)-C(2)-C(1)	112.9(4)
N(2)-C(2)-H(2A)	109.0(2)
C(1)-C(2)-H(2A)	109.0(2)
N(2)-C(2)-H(2B)	109.0(2)
C(1)-C(2)-H(2B)	109.0(3)
H(2A)-C(2)-H(2B)	107.8
C(2)-N(2)-C(3)	113.4(3)
C(2)-N(2)-H(21)	107(4)
C(3)-N(2)-H(21)	105(4)
C(2)-N(2)-H(2)	108(3)
C(3)-N(2)-H(2)	107(3)
H(21)-N(2)-H(2)	117(5)
N(2)-C(3)-C(4)	112.1(3)
N(2)-C(3)-H(3A)	109.2(2)
C(4)-C(3)-H(3A)	109.2(2)
N(2)-C(3)-H(3B)	109.2(2)
C(4)-C(3)-H(3B)	109.2(2)
H(3A)-C(3)-H(3B)	107.9
N(3)-C(4)-C(3)	113.7(3)
N(3)-C(4)-H(4A)	108.8(2)
C(3)-C(4)-H(4A)	108.8(2)
N(3)-C(4)-H(4B)	108.8(2)
C(3)-C(4)-H(4B)	108.8(2)
H(4A)-C(4)-H(4B)	107.7
C(4)-N(3)-C(11)#1	111.3(3)
C(4)-N(3)-H(31)	116(3)
C(11)#1-N(3)-H(31)	107(3)
C(4)-N(3)-H(3)	111(4)
C(11)#1-N(3)-H(3)	112(4)
H(31)-N(3)-H(3)	99(5)
N(3)#1-C(11)-C(12)	110.7(3)
N(3)#1-C(11)-H(11A)	109.5(2)
C(12)-C(11)-H(11A)	109.5(2)
N(3)#1-C(11)-H(11B)	109.5(2)
C(12)-C(11)-H(11B)	109.5(2)
H(11A)-C(11)-H(11B)	108.1
N(1)-C(12)-C(11)	112.7(3)
N(1)-C(12)-H(12A)	109.1(2)
C(11)-C(12)-H(12A)	109.1(2)
N(1)-C(12)-H(12B)	109.1(2)
C(11)-C(12)-H(12B)	109.1(2)
H(12A)-C(12)-H(12B)	107.8
N(6)#2-C(5)-C(6)	111.2(4)
N(6)#2-C(5)-H(5A)	109.4(2)
C(6)-C(5)-H(5A)	109.4(3)
N(6)#2-C(5)-H(5B)	109.4(2)
C(6)-C(5)-H(5B)	109.4(2)
H(5A)-C(5)-H(5B)	108.0

N(4)-C(6)-C(5)	112.8(4)
N(4)-C(6)-H(6A)	109.0(3)
C(5)-C(6)-H(6A)	109.1(3)
N(4)-C(6)-H(6B)	109.0(2)
C(5)-C(6)-H(6B)	109.0(2)
H(6A)-C(6)-H(6B)	107.8
C(14)-N(4)-C(6)	111.6(4)
C(14)-N(4)-C(7)	112.7(4)
C(6)-N(4)-C(7)	109.7(4)
N(4)-C(14)-H(14A)	109.5(3)
N(4)-C(14)-H(14B)	109.5(3)
H(14A)-C(14)-H(14B)	109.5
N(4)-C(14)-H(14C)	109.5(3)
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(4)-C(7)-C(8)	112.3(4)
N(4)-C(7)-H(7A)	109.1(2)
C(8)-C(7)-H(7A)	109.2(3)
N(4)-C(7)-H(7B)	109.1(3)
C(8)-C(7)-H(7B)	109.2(3)
H(7A)-C(7)-H(7B)	107.9
C(7)-C(8)-N(5)	112.9(4)
C(7)-C(8)-H(8A)	109.0(3)
N(5)-C(8)-H(8A)	109.0(2)
C(7)-C(8)-H(8B)	109.0(3)
N(5)-C(8)-H(8B)	109.0(3)
H(8A)-C(8)-H(8B)	107.8
C(9)-N(5)-C(8)	113.6(4)
C(9)-N(5)-H(51)	103(4)
C(8)-N(5)-H(51)	111(4)
C(9)-N(5)-H(5)	110(3)
C(8)-N(5)-H(5)	108(3)
H(51)-N(5)-H(5)	112(5)
N(5)-C(9)-C(10)	113.3(4)
N(5)-C(9)-H(9A)	108.9(2)
C(10)-C(9)-H(9A)	108.9(2)
N(5)-C(9)-H(9B)	108.9(2)
C(10)-C(9)-H(9B)	108.9(3)
H(9A)-C(9)-H(9B)	107.7
N(6)-C(10)-C(9)	113.7(4)
N(6)-C(10)-H(10A)	108.8(2)
C(9)-C(10)-H(10A)	108.8(2)
N(6)-C(10)-H(10B)	108.8(2)
C(9)-C(10)-H(10B)	108.8(3)
H(10A)-C(10)-H(10B)	107.7
C(10)-N(6)-C(5)#2	111.5(3)
C(10)-N(6)-H(61)	109(4)
C(5)#2-N(6)-H(61)	116(4)
C(10)-N(6)-H(6)	112(4)
C(5)#2-N(6)-H(6)	106(4)
H(61)-N(6)-H(6)	103(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z #2 -x+1,-y+1,-z+1

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $C_{14}H_{54}N_6O_{20}P_4$.

	U11	U22	U33	U23	U13	U12
O(15)	60(2)	54(2)	60(2)	9(2)	32(2)	19(2)
O(16)	80(3)	56(2)	45(2)	8(2)	19(2)	-13(2)
O(17)	85(3)	82(3)	51(2)	26(2)	34(2)	47(2)
O(18)	140(10)	69(6)	75(7)	34(5)	12(7)	0(7)
O(18')	272(29)	52(9)	59(10)	18(8)	47(16)	55(15)
O(19)	83(3)	93(3)	73(3)	51(3)	35(2)	19(2)
O(20)	138(5)	161(6)	118(4)	81(4)	91(4)	65(4)
P(1)	31(1)	29(1)	23(1)	11(1)	9(1)	5(1)
O(1)	44(2)	36(2)	36(2)	17(1)	14(1)	-3(1)
O(2)	41(2)	43(2)	38(2)	19(1)	20(1)	15(1)
O(3)	41(2)	40(2)	31(2)	10(1)	11(1)	0(1)
O(4)	41(2)	48(2)	35(2)	24(2)	18(1)	17(1)
P(2)	33(1)	32(1)	29(1)	14(1)	11(1)	7(1)
O(5)	39(2)	38(2)	53(2)	25(2)	14(2)	9(1)
O(6)	53(2)	49(2)	36(2)	13(2)	23(2)	9(2)
O(7)	39(2)	38(2)	42(2)	17(2)	3(2)	-1(1)
P(3)	28(1)	26(1)	19(1)	5(1)	6(1)	4(1)
O(8)	40(2)	24(1)	24(1)	6(1)	14(1)	4(1)
O(9)	31(2)	30(1)	21(1)	3(1)	4(1)	2(1)
P(4)	31(1)	25(1)	22(1)	4(1)	6(1)	5(1)
O(10)	43(2)	37(2)	33(2)	14(1)	11(1)	10(1)
O(11)	31(2)	53(2)	29(2)	13(2)	10(1)	-4(1)
O(12)	32(2)	29(2)	33(2)	8(1)	3(1)	-2(1)
O(13)	42(2)	44(2)	34(2)	9(1)	17(1)	13(2)
O(14)	40(2)	47(2)	30(2)	19(2)	6(1)	3(1)
N(1)	33(2)	26(2)	30(2)	2(2)	10(2)	1(2)
C(13)	35(2)	53(3)	50(3)	19(2)	13(2)	5(2)
C(1)	44(3)	38(2)	28(2)	3(2)	15(2)	6(2)
C(2)	47(3)	42(2)	33(2)	13(2)	21(2)	9(2)
N(2)	38(2)	31(2)	23(2)	9(2)	11(2)	4(2)
C(3)	30(2)	43(2)	26(2)	7(2)	6(2)	0(2)
C(4)	33(2)	38(2)	35(2)	18(2)	9(2)	10(2)
N(3)	27(2)	31(2)	30(2)	11(2)	9(2)	7(2)
C(11)	39(2)	31(2)	47(3)	11(2)	21(2)	11(2)
C(12)	43(3)	27(2)	39(2)	-1(2)	20(2)	0(2)
C(5)	45(3)	40(2)	30(2)	13(2)	15(2)	19(2)
C(6)	56(3)	32(2)	35(2)	13(2)	16(2)	14(2)
N(4)	55(2)	33(2)	32(2)	10(2)	17(2)	9(2)
C(14)	68(4)	64(4)	37(3)	13(3)	9(3)	9(3)
C(7)	65(3)	39(3)	48(3)	20(2)	26(3)	9(2)
C(8)	65(3)	48(3)	45(3)	28(2)	29(3)	17(2)
N(5)	41(2)	33(2)	29(2)	14(2)	12(2)	6(2)
C(9)	39(2)	44(3)	38(2)	17(2)	6(2)	-1(2)
C(10)	39(2)	49(3)	39(2)	19(2)	18(2)	10(2)
N(6)	38(2)	31(2)	21(2)	6(2)	9(2)	10(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $C_{14}H_{54}N_6O_{20}P_4$.

	x/a	y/b	z/c	U(eq)
H(11)	4025(57)	2116(48)	1230(54)	64(17)
H(14)	2000(58)	3693(47)	1236(50)	61(17)
H(21)	-1128(72)	-1860(62)	1351(62)	97(23)
H(2)	-1390(45)	-920(36)	750(42)	34(11)
H(31)	1209(56)	-726(50)	140(48)	61(16)
H(3)	18(62)	-1463(46)	-363(50)	58(16)
H(51)	4768(64)	5299(55)	7955(58)	78(19)
H(5)	5507(60)	4911(48)	7019(50)	66(17)
H(61)	4731(73)	6101(55)	6001(60)	84(20)
H(6)	3487(48)	5672(40)	5001(45)	30(13)
H(13A)	-3604(5)	-4(10)	706(28)	74(8)
H(13B)	-3570(5)	848(29)	151(16)	74(8)
H(13C)	-3665(5)	1220(20)	1358(14)	74(8)
H(1A)	-1812(5)	1135(4)	3014(4)	52(3)
H(1B)	-395(5)	1088(4)	3000(4)	52(3)
H(2A)	-1104(5)	-544(4)	3002(4)	52(3)
H(2B)	-2487(5)	-711(4)	1955(4)	52(3)
H(3A)	913(4)	-692(4)	2687(4)	52(3)
H(3B)	681(4)	-35(4)	1882(4)	52(3)
H(4A)	2008(4)	-1485(4)	1617(4)	52(3)
H(4B)	642(4)	-2296(4)	964(4)	52(3)
H(11A)	-2403(5)	2187(3)	144(4)	52(3)
H(11B)	-1025(5)	2993(3)	836(4)	52(3)
H(12A)	-347(5)	2267(3)	2247(4)	52(3)
H(12B)	-1744(5)	2602(3)	2115(4)	52(3)
H(5A)	7743(5)	3060(4)	4942(4)	52(3)
H(5B)	6612(5)	2383(4)	3690(4)	52(3)
H(6A)	5138(5)	2206(4)	4479(4)	52(3)
H(6B)	6435(5)	1776(4)	5066(4)	52(3)
H(14A)	7793(14)	2682(8)	7097(23)	74(8)
H(14B)	7677(11)	3887(23)	7757(9)	74(8)
H(14C)	8210(7)	3622(29)	6783(16)	74(8)
H(7A)	5488(6)	2185(4)	6684(5)	52(3)
H(7B)	4374(6)	2537(4)	5782(5)	52(3)
H(8A)	5887(6)	3844(4)	8153(4)	52(3)
H(8B)	4346(6)	3394(4)	7566(4)	52(3)
H(9A)	2796(5)	4186(4)	6402(4)	52(3)
H(9B)	3451(5)	4090(4)	5533(4)	52(3)
H(10A)	2108(5)	5528(4)	5824(4)	52(3)
H(10B)	3346(5)	6163(4)	7015(4)	52(3)

Table S12. Weighted least-squares planes through the starred atoms for $C_{14}H_{54}N_6O_{20}P_4$.
(Nardelli, Musatti, Domiano & Andreetti Ric.Sci.(1965),15(II-A),807).
Equation of the plane: m1*X+m2*Y+m3*Z=d

Plane 1
m1 = -0.52003(0.00057)
m2 = -0.22475(0.00088)
m3 = -0.82405(0.00037)
D = 0.00000(0.00141)

Atom	d	s	d/s	(d/s)**2
N1 *	-0.0703	0.0036	-19.799	391.986
N2 *	0.0680	0.0036	18.904	357.366
N3 *	-0.1057	0.0038	-27.679	766.141
N1S *	0.0703	0.0036	19.799	391.986
N2S *	-0.0680	0.0036	-18.904	357.366
N3S *	0.1057	0.0038	27.679	766.141

Plane 2
m1 = -0.60687(0.00071)
m2 = -0.47415(0.00067)
m3 = -0.63788(0.00061)
D = -7.34433(0.00249)

Atom	d	s	d/s	(d/s)**2
N4 *	0.0817	0.0041	19.783	391.364
N5 *	-0.0735	0.0040	-18.233	332.453
N6 *	0.1131	0.0043	26.285	690.922
N4S *	-0.0817	0.0041	-19.783	391.367
N5S *	0.0735	0.0040	18.233	332.455
N6S *	-0.1131	0.0043	-26.285	690.921

Dihedral angles formed by LSQ-planes

Plane - plane		angle (e.s.d.)
1	2	18.59(0.06)

Table S13. Thermodynamic Parameters for the Protonation of Hexa- and Hepta-aza Macrocyclic Polyamines in 0.15 mol dm^{-3} $NaClO_4$ at 298.1±0.1 K.

Log K

	L1	L2	L3	L4	L5
$L+H^+ = LH^+$	10.15(1)[a]	9.81(1)	9.75(1)	9.76(1)	9.27(1)
$LH^+ + H^+ = LH_2^{2+}$	9.48(1)	9.41(1)	9.11(1)	9.28(1)	8.95(1)
$LH_2^{2+} + H^+ = LH_3^{3+}$	8.89(1)	8.04(1)	7.53(1)	8.63(1)	7.97(1)
$LH_3^{3+} + H^+ = LH_4^{4+}$	4.27(1)	3.88(1)	2.59(2)	6.42(1)	5.42(1)
$LH_4^{4+} + H^+ = LH_5^{5+}$	2.21(2)			3.73	2.98(1)
$LH_5^{5+} + H^+ = LH_6^{6+}$	1.0(1)			2.13(3)	1.78(1)
$LH_6^{6+} + H^+ = LH_7^{7+}$				2.0(1)	

ΔH° (kcal mol^{-1})

	L1	L2	L3	L4	L5
$L+H^+ = LH^+$	-8.28(5)	-8.5(1)	-8.30(8)	-8.87(7)	-7.79(5)
$LH^+ + H^+ = LH_2^{2+}$	-10.82(6)	-10.4(1)	-10.32(9)	-10.16(8)	-9.91(5)
$LH_2^{2+} + H^+ = LH_3^{3+}$	-11.88(6)	-9.9(1)	-10.13(9)	-10.75(6)	-9.84(6)
$LH_3^{3+} + H^+ = LH_4^{4+}$	-12.12(8)	-12.3(2)	-4.4(2)	-11.11(7)	-10.27(7)
$LH_4^{4+} + H^+ = LH_5^{5+}$	-3.4(2)			-8.82(9)	-7.9(1)
$LH_5^{5+} + H^+ = LH_6^{6+}$				-8.4(2)	-10.1(1)

$T\Delta S^\circ$ (kcal mol^{-1})

	L1	L2	L3	L4	L5
$L+H^+ = LH^+$	5.56(5)	4.8(1)	5.00(9)	4.44(7)	4.9(1)
$LH^+ + H^+ = LH_2^{2+}$	2.12(6)	2.0(1)	2.1(1)	2.50(8)	2.3(1)
$LH_2^{2+} + H^+ = LH_3^{3+}$	0.24(5)	0.7(1)	0.14(9)	1.03(6)	1.0(1)
$LH_3^{3+} + H^+ = LH_4^{4+}$	-6.29(8)	-7.1(2)	-0.9(2)	-2.35(7)	-2.9(1)
$LH_4^{4+} + H^+ = LH_5^{5+}$	-0.3(2)			-3.73(9)	-3.9(1)
$LH_5^{5+} + H^+ = LH_6^{6+}$				-5.5(2)	-7.5(1)

a) Values in parentheses are standard deviation on the last significant figure.

Table S14. Thermodynamic Parameters for the Protonation of Paracyclophane in 0.15 mol dm^{-3} $NaClO_4$ at 298.1±0.1 K

Log K

	L6	**L7**	**L8**	**L9**[a]
$L+H^+ = LH^+$	9.93(2)[b]	10.59(2)	10.39(2)	8.93(1)
$LH^+ + H^+ = LH_2^{2+}$	9.09(2)	9.62(2)	9.54(2)	8.22(1)
$LH_2^{2+} + H^+ = LH_3^{3+}$	7.44(2)	7.72(2)	7.54(2)	7.35(1)
$LH_3^{3+} + H^+ = LH_4^{4+}$	3.61(2)	6.08(2)	6.64(2)	6.44(1)
$LH_4^{4+} + H^+ = LH_5^{5+}$				1.5(1)

ΔH° (kcal mol^{-1})

	L6	**L7**	**L8**	**L9**[a]
$L+H^+ = LH^+$	-9.55(2)	-10.07(2)	-10.68(2)	-6.31(2)
$LH^+ + H^+ = LH_2^{2+}$	-10.91(2)	-11.43(2)	-10.65(2)	-6.79(2)
$LH_2^{2+} + H^+ = LH_3^{3+}$	-10.70(2)	-10.97(2)	-11.50(2)	-10.16(3)
$LH_3^{3+} + H^+ = LH_4^{4+}$	-7.01(2)	-10.65(2)	-13.00(2)	-11.71(3)

$T\Delta S^\circ$ (kcal mol^{-1})

	L6	**L7**	**L8**	**L9**[a]
$L+H^+ = LH^+$	4.00(5)	4.38(5)	3.50(5)	5.87(2)
$LH^+ + H^+ = LH_2^{2+}$	1.50(5)	1.70(5)	2.36(5)	4.43(4)
$LH_2^{2+} + H^+ = LH_3^{3+}$	-0.60(5)	-0.44(5)	-1.21(5)	-0.14(4)
$LH_3^{3+} + H^+ = LH_4^{4+}$	-2.10(8)	-2.35(8)	-3.94(8)	-2.92(5)

a) Values obtained in 0.15 mol dm^{-3} $NaClO_4$ at 298.1□0.1 K.

b) Values in parentheses are standard deviation on the last significant figure.

Table S15. Thermodynamic Parameters for the Protonation of Acyclic Polyamines in 0.15 mol dm^{-3} $NaClO_4$ at 298.1±0.1 K

Log K

	L10	**L11**	**L12**	**L13**	**L14**
$L+H^+ = LH^+$	10.28(2)[a]	10.22(1)	10.36(5)	10.27(4)	10.35(9)
$LH^++H^+ = LH_2^{2+}$	9.52(1)	9.60(1)	9.86(2)	9.93(2)	10.24(3)
$LH_2^{2+}+H^+ = LH_3^{3+}$	8.84(1)	8.93(1)	8.40(4)	8.60(3)	8.97(5)
$LH_3^{3+}+H^+ = LH_4^{4+}$	6.54(1)	8.05(1)	5.65(6)	7.29(3)	7.99(5)
$LH_4^{4+}+H^+ = LH_5^{5+}$	3.81(1)	4.75(1)			
$LH_5^{5+}+H^+ = LH_6^{6+}$	2.51(2)	3.73(2)			
$LH_6^{6+}+H^+ = LH_7^{7+}$		2.84(2)			

ΔH° (kcal mol^{-1})

	L10	**L11**	**L12**	**L13**	**L14**
$L+H^+ = LH^+$	-9.54(1)	-9.74(1)	-12.30(2)	-12.34(2)	-12.60(2)
$LH^++H^+ = LH_2^{2+}$	-10.31(1)	-9.98(1)	-12.70(2)	-12.60(2)	-12.47(2)
$LH_2^{2+}+H^+ = LH_3^{3+}$	-10.62(1)	-10.36(1)	-11.17(3)	-12.43(3)	-12.68(3)
$LH_3^{3+}+H^+ = LH_4^{4+}$	-9.70(1)	-11.15(2)	-9.62(3)	-11.29(3)	-12.22(3)
$LH_4^{4+}+H^+ = LH_5^{5+}$	-7.58(1)	-8.06(4)			
$LH_5^{5+}+H^+ = LH_6^{6+}$	-8.23(4)	-7.70(5)			
$LH_6^{6+}+H^+ = LH_7^{7+}$		-8.10(4)			

$T\Delta S^\circ$ (kcal mol^{-1})

	L10	**L11**	**L12**	**L13**	**L14**
$L+H^+ = LH^+$	4.48(1)	4.20(1)	1.83(3)	1.66(3)	1.52(5)
$LH^++H^+ = LH_2^{2+}$	2.68(1)	3.11(3)	0.75(5)	0.95(4)	1.51(7)
$LH_2^{2+}+H^+ = LH_3^{3+}$	1.44(3)	1.83(3)	0.29(6)	-0.06(6)	-0.45(8)
$LH_3^{3+}+H^+ = LH_4^{4+}$	-0.77(5)	-0.17(5)	-1.90(6)	-1.35(5)	-1.32(9)
$LH_4^{4+}+H^+ = LH_5^{5+}$	-2.38(5)	-1.58(5)			
$LH_5^{5+}+H^+ = LH_6^{6+}$	-4.80(6)	-3.09(4)			
$LH_6^{6+}+H^+ = LH_7^{7+}$		-4.84(5)			

a) Values in parentheses are standard deviation on the last significant figure.

Table S16. Thermodynamic Parameters for the Protonation of PO_4^{3-} and $P_2O_7^{4-}$ Anions Determined in 0.15 mol dm^{-3} $NaClO_4$ at 298.1±0.1 K

	log K	ΔH° (kcal mol^{-1})	$T\Delta S^\circ$ (kcal mol^{-1})
$PO_4^{3-} + H^+ = HPO_4^{2-}$	11.54(1)[a]	-4.57(5)	11.17(5)
$HPO_4^{2-} + H^+ = H_2PO_4^-$	6.72(1)	-0.99(6)	8.18(6)
$H_2PO_4^- + H^+ = H_3PO_4$	2.11(1)	1.84(8)	4.72(8)
$P_2O_7^{4-} + H^+ = HP_2O_7^{3-}$	8.138(3)	-0.37(4)	10.73(4)
$HP_2O_7^{3-} + H^+ = H_2P_2O_7^{2-}$	5.92(1)	-0.13(6)	7.95(6)
$H_2P_2O_7^{2-} + H^+ = H_3P_2O_7^-$	1.94(1)	2.61(9)	5.25(9)

a) Values in parentheses are standard deviation on the last significant figure.