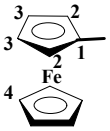
Electronic Supplementary Material (ESI) for New Journal of Chemistry.

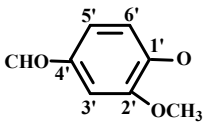
Phosphorus-nitrogen compounds: Part 63. Mono and Bis-vanillinatobisferrocenyldi-spiro(N/N)cyclotriphosphazenes and Their Macrocyclic Schiff-Bases: Synthesis, Structural Characterization and Isomerism

Yasemin Tümer, Nuran Asmafiliz, Zeynel Kılıç, Tuncer Hökelek

Supplementary Materials

Table S1 ^{13}C (decoupled) NMR spectral data of the dispirophosphazenes. [Chemical shifts (δ) reported in ppm and *J* values in Hz].

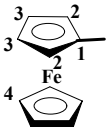


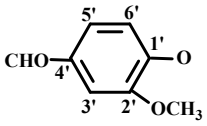


	6	7	9	10	11	12	13	14
N<u>C</u>H$_3$	-	-	-	-	31.60 31.65	-	31.41 31.94	-
N<u>C</u>H$_2$CH$_3$	39.23	39.27 $^2J_{PC}$= 4.1 39.38 $^2J_{PC}$= 4.4	38.90	39.01	-	39.20	-	38.88
NCH$_2$<u>C</u>H$_3$	14.11 $^3J_{PC}$=2.9 14.13 $^3J_{PC}$=3.0	14.08 $^3J_{PC}$=5.3 14.15 $^3J_{PC}$=5.2	13.88 $^3J_{PC}$=3.1 13.91 $^3J_{PC}$=3.1	13.89 $^3J_{PC}$=2.8	-	14.16	-	13.90
CH$_3$N<u>C</u>H$_2$	-	-	-	-	43.85 $^2J_{PC}$=12.2 43.84	-	42.09	-
C$_2$H$_5$N<u>C</u>H$_2$	43.09 $^2J_{PC}$=12.8 43.54 $^2J_{PC}$=13.0	43.60 $^2J_{PC}$=9.7 43.62 $^2J_{PC}$=12.4	43.44 $^2J_{PC}$=12.9 43.45	43.63 $^2J_{PC}$=13.1 43.64	-	43.50	-	43.42
NCH$_2$<u>C</u>H$_2$	-	-	-	-	28.60 28.91	28.77 29.43	29.38 29.48	29.68 30.32
N<u>C</u>H$_2$	43.55 44.10	44.09 $^2J_{PC}$= 12.6 44.11 $^2J_{PC}$= 12.6	44.58 $^2J_{PC}$= 12.9 44.59	43.81 $^2J_{PC}$= 13.2 43.82	44.23 (spiro) 61.43 61.50 (Schiff-base)	43.97 (spiro) 61.47 (Schiff-base)	44.16 44.41 (spiro) 61.27 61.50 (Schiff-base)	44.10 (spiro) 62.53 (Schiff-base)
Fc<u>C</u>H$_2$	44.24	44.04	44.19	44.18	47.25 $^2J_{PC}$=6.0 47.29 $^2J_{PC}$=6.0	44.20	47.23	44.49
C4	68.38	68.41 68.44	68.55	68.58	68.36	68.37	68.52	68.52

C3	68.05 68.07	68.01 68.09 68.17	67.72 67.97	67.78 68.37	67.91 67.96 67.99 68.03	67.99	67.71 67.92	67.44 67.90
C2	69.31 69.41	69.22 69.50 69.71 70.01	68.62	69.46 69.54	69.41 69.66 69.75	69.47 69.71	69.91 69.98	68.77
C1	83.96 $^3J_{PC}$=4.9 84.00 $^3J_{PC}$=5.0	83.52 $^3J_{PC}$=8.7 83.80 $^3J_{PC}$=8.2	84.76 $^3J_{PC}$=4.5 84.80 $^3J_{PC}$=4.5	83.99 $^3J_{PC}$=3.9 84.02 $^3J_{PC}$=3.9	84.09 $^3J_{PC}$=4.5 84.10 $^3J_{PC}$=4.5	84.05	84.74	84.84
O<u>C</u>H$_3$	56.19	56.19	55.94 56.22	56.08	56.17 56.28	56.33	55.93 56.33	55.96 56.31
<u>C</u>HO	191.05	191.10	191.08 191.17	191.19	-	-	-	-
<u>C</u>HN	-	-	-	-	160.30 160.34	160.30	160.32 160.49	160.38
C6'	121.92 $^3J_{PC}$=2.5	122.67 $^3J_{PC}$=3.0	121.70 $^3J_{PC}$=2.6 122.14 $^3J_{PC}$=2.6	122.65 $^3J_{PC}$=3.4	121.76 $^3J_{PC}$=6.0 121.88 $^3J_{PC}$=6.0	121.81	121.89 121.96	121.91
C5'	124.80	124.68	124.87	124.72	124.83	124.86	125.53	125.51
C4'	133.20	133.97	133.08 133.29	134.01	133.04 133.10	133.01	132.94 133.05	133.18
C3'	110.86	111.07	110.49 110.87	110.89	110.58	110.61	110.12 110.61	110.32
C2'	146.27 $^3J_{PC}$=7.5	145.36 $^3J_{PC}$=8.7	146.10 $^3J_{PC}$=7.5 146.30 $^3J_{PC}$=7.4	145.36 $^3J_{PC}$=9.2	143.14 $^3J_{PC}$=7.6 143.20 $^3J_{PC}$=12.1	143.31 $^3J_{PC}$=10.4	142.94 142.96	143.86
C1'	151.82 $^2J_{PC}$ = 6.9	152.01 $^2J_{PC}$=6.3	151.64 $^2J_{PC}$ = 7.3 151.90 $^2J_{PC}$ = 6.6	152.15 $^2J_{PC}$=6.2	151.56 $^2J_{PC}$ = 6.0 151.67 $^2J_{PC}$ = 6.0	151.65	151.42 151.64	151.55

Table S2 ^{1}H NMR spectral data of the dispirophosphazenes. [Chemical shifts (δ) reported in ppm and *J* values in Hz]. [d: doublet, t: triplet, m: multiplet, bp: broad peak and dd: doublet of doublets].





	6	**7**	**9**	**10**	**11**	**12**	**13**	**14**
NC<u>H</u>$_3$	-	-	-	-	2.45 (d, 3H) $^3J_{PH}$= 4.8 2.51 (d, 3H) $^3J_{PH}$= 6.0	-	2.38 (3H)	-
NC<u>H</u>$_2$CH$_3$	2.85 (m, 4H) $^3J_{HH}$= 7.2 $^3J_{PH}$= 6.3	2.92 (m, 4H) $^3J_{HH}$= 7.2 $^3J_{PH}$= 7.0	2.71 (m, 2H) $^3J_{HH}$= 7.2 $^3J_{PH}$= 6.5 2.81 (m, 2H) $^3J_{HH}$= 7.2 $^3J_{PH}$= 6.5	2.82 (m, 4H) $^3J_{HH}$= 7.0 $^3J_{PH}$= 7.6	-	2.72-3.12 (m, 4H)	-	2.68 (m, 4H)
NCH$_2$C<u>H</u>$_3$	1.13 (t, 6H) $^3J_{HH}$= 7.2	1.18 (t, 3H) $^3J_{HH}$= 7.2 1.30 (t, 3H) $^3J_{HH}$= 7.2	1.04 (t, 6H) $^3J_{HH}$= 7.2	1.09 (t, 6H) $^3J_{HH}$= 7.0	-	1.09 (m, 6H)	-	1.25 (m, 6H)
CH$_3$NC<u>H</u>$_2$	-	-	-	-	3.00-3.05 (m, 4H)	-	3.03-3.11 (m, 4H)	-
C$_2$H$_5$NC<u>H</u>$_2$	3.04-3.12 (m, 4H)	3.02-3.18 (m, 4H)	3.07-3.22 (m, 4H)	3.05-3.14 (m, 4H)	-	2.72-3.12 (m, 4H)	-	2.68 (m, 4H)
NCH$_2$C<u>H</u>$_2$	-	-	-	-	1.73 (m, 4H)	1.75 (m, 4H)	1.76 (m, 4H)	1.73 (m, 4H)
NC<u>H</u>$_2$	3.04-3.12 (m, 4H)	3.02-3.18 (m, 4H)	3.07-3.22 (m, 4H)	3.05-3.14 (m, 4H)	3.00-3.05 (m, 4H) (spiro) 3.61-3.66 (m, 4H) (Schiff-base)	2.72-3.12 (m, 4H) (spiro) 3.64 (bp, 4H) (Schiff-base)	3.03-3.11 (m, 4H) (spiro) 3.47-3.65 (m, 4H) (Schiff-base)	3.12 (m, 4H) (spiro) 3.12 (m, 4H) (Schiff-base)
FcC<u>H</u>$_2$	3.67 $^3J_{PH}$= 7.5 $^2J_{HH}$= 11.5 (dd, 2H) 3.68 $^3J_{PH}$= 7.6 $^2J_{HH}$= 11.5 (dd, 2H)	3.69 $^3J_{PH}$= 7.8 $^2J_{HH}$= 14.3 (dd, 2H) 3.77 $^3J_{PH}$= 7.3 $^2J_{HH}$= 14.3 (dd, 2H)	3.61 $^3J_{PH}$= 7.5 $^2J_{HH}$= 14.8 (dd, 1H) 3.64 $^3J_{PH}$= 7.5 $^2J_{HH}$= 14.8 (dd, 1H) 3.73 $^3J_{PH}$= 8.0 $^2J_{HH}$= 14.7 (dd, 1H) 3.76 $^3J_{PH}$= 8.1 $^2J_{HH}$= 14.7 (dd, 1H)	3.78 $^3J_{PH}$= 8.3 $^2J_{HH}$= 14.2 (dd, 2H) 3.81 $^3J_{PH}$= 8.3 $^2J_{HH}$= 14.2 (dd, 2H)	3.74 $^3J_{PH}$= 6.6 $^2J_{HH}$= 9.0 (dd, 2H) 3.75 $^3J_{PH}$= 6.6 $^2J_{HH}$= 9.0 (dd, 2H)	3.64 (bp, 4H)	3.80 (m, 4H)	3.63 (bp, 4H)

H4	4.03 (bp, 10H)	4.10 (bp, 10H)	4.05 (bp, 10H)	4.15 (bp, 10H)	3.99 4.00 (bp, 10H)	4.02 (bp, 10H)	4.03 4.04 (bp, 10H)	4.04 (bp, 10H)
H3	4.04 (bp, 4H)	4.03 (bp, 4H)	4.06 4.08 (bp, 4H)	4.12 (bp, 4H)	4.02 4.03 (bp, 4H)	3.90 (bp, 4H)	4.12 4.13 (bp, 4H)	3.91 (bp, 4H)
H2	4.08 (bp, 4H)	4.18 4.19 (bp, 4H)	4.14 (bp, 4H)	4.20 (bp, 4H)	4.09 4.15 (bp, 4H)	4.12 (bp, 4H)	4.18 (bp, 4H)	4.10 (bp, 4H)
O$C\underline{H}_3$	3.90 (s, 6H)	3.93 (s, 3H)	3.85 3.92 (s, 6H)	3.90 (s, 3H)	3.83 3.88 (s, 6H)	3.86 (s, 6H)	3.91 (s, 6H)	3.82 (s, 6H)
C$\underline{H}$O	9.94 (s, 2H)	9.95 (s, 1H)	9.89 9.92 (s, 2H)	9.95 (s, 1H)	-	-	-	-
C$\underline{H}$N	-	-	-	-	8.18 8.20 (s, 2H)	8.22 (s, 2H)	8.19 (s, 2H)	8.20 (s, 2H)
H6'	7.98 $^3J_{HH}$= 8.2 (d, 2H)	7.86 $^3J_{HH}$= 8.1 (d, 1H)	7.93 $^3J_{HH}$= 8.2 (d, 1H) 7.88 $^3J_{HH}$= 8.0 (d, 1H)	7.82 $^3J_{HH}$= 8.1 (d, 1H)	7.77 $^3J_{HH}$= 8.4 (d, 1H) 7.79 $^3J_{HH}$= 8.4 (d, 1H)	7.83 (bp, 2H)	7.69 $^3J_{HH}$= 8.4 (d, 1H) 7.80 $^3J_{HH}$= 7.8 (d, 1H)	7.85 (bp, 2H)
H5'	7.46 $^3J_{HH}$= 8.2 $^4J_{HH}$= 1.9 (m, 2H)	7.46 $^3J_{HH}$= 8.1 $^4J_{HH}$= 1.5 (m, 1H)	7.30 $^3J_{HH}$= 8.2 (d, 1H) 7.31 $^3J_{HH}$= 8.0 (d, 1H)	7.47 $^3J_{HH}$= 8.1 (d, 1H)	7.14 $^3J_{HH}$= 8.4 (d, 1H) 7.17 $^3J_{HH}$= 8.4 (d, 1H)	7.29 (bp, 2H)	7.09 $^3J_{HH}$= 8.4 (d, 1H) 7.11 $^3J_{HH}$= 7.8 (d, 1H)	7.29 (bp, 2H)
H3'	7.48 $^4J_{HH}$= 1.9 (d, 2H)	7.51 $^4J_{HH}$= 1.5 (d, 1H)	7.42 7.44 (s, 2H)	7.49 (s, 1H)	7.40 7.44 (s, 2H)	7.46 (s, 2H)	7.36 7.44 (s, 2H)	7.46 (s, 2H)

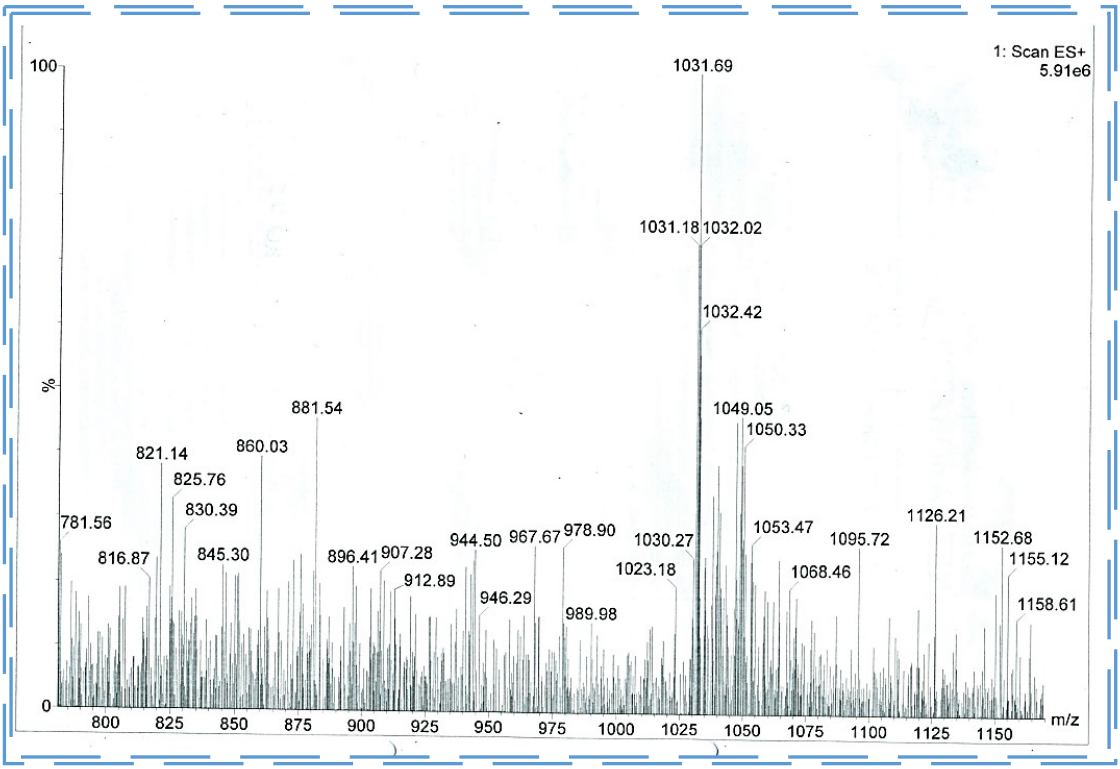


Fig. S1 The ESI-MS spectrum of compound **12**.

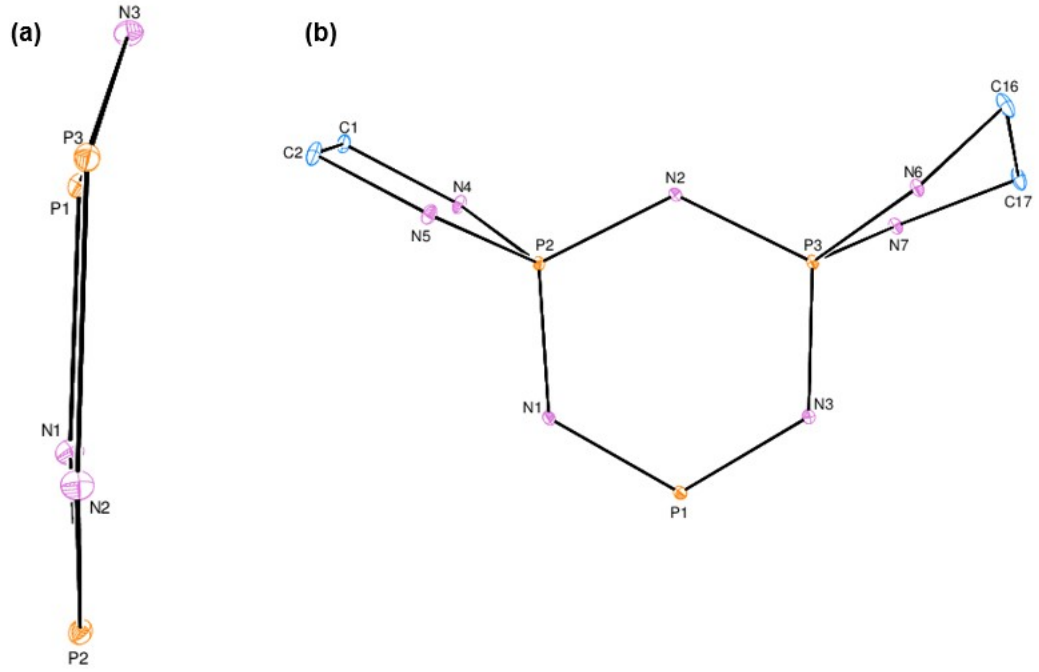


Fig. S2 The conformations of (a) the phosphazene ring and (b) the five-membered spiro-ring of **6**.

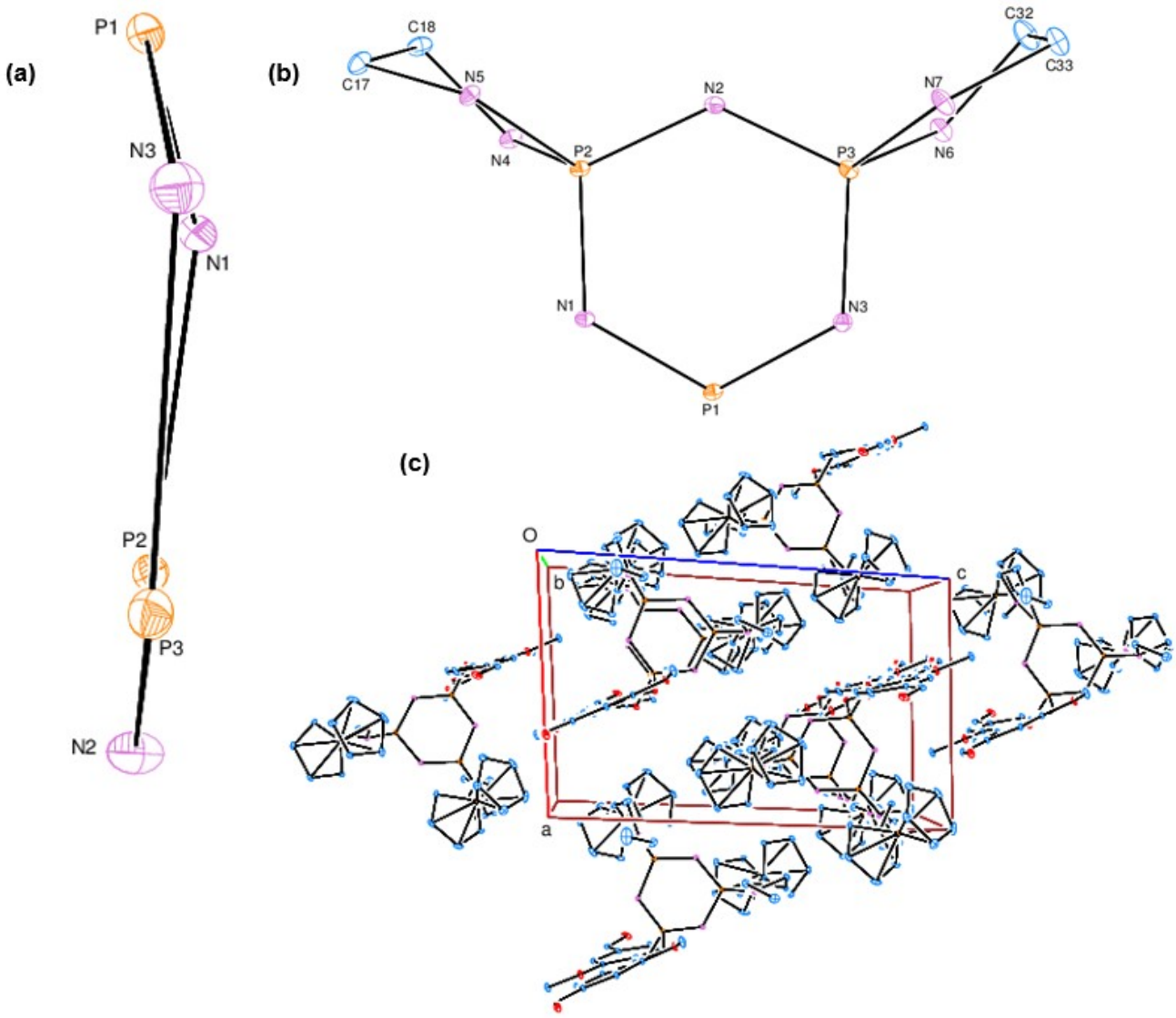


Fig. S3 The conformations of (a) the phosphazene ring and (b) the five-membered spiro-ring of **9**.

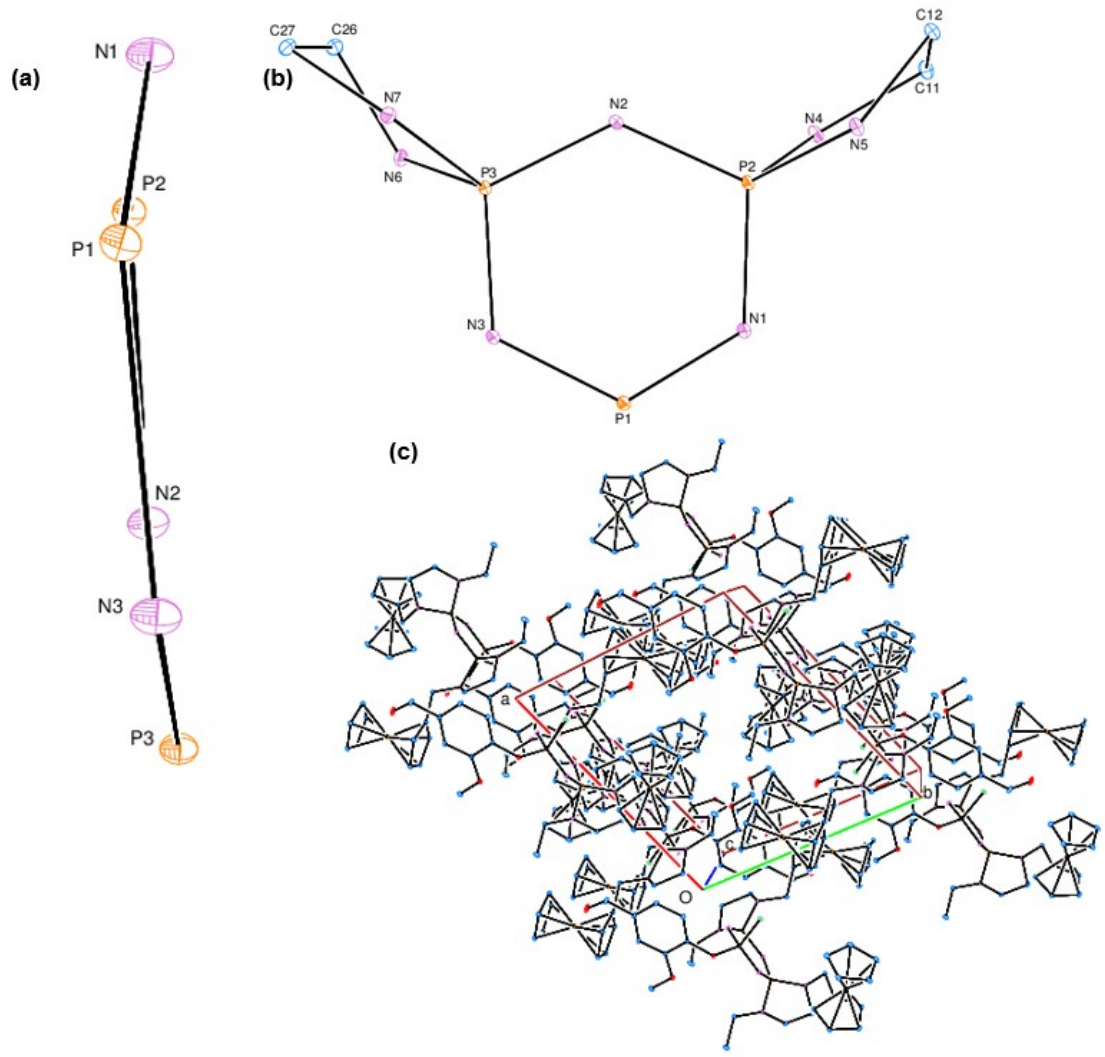


Fig. S4 The conformations of (a) the phosphazene ring and (b) the five-membered spiro-ring of **10**.

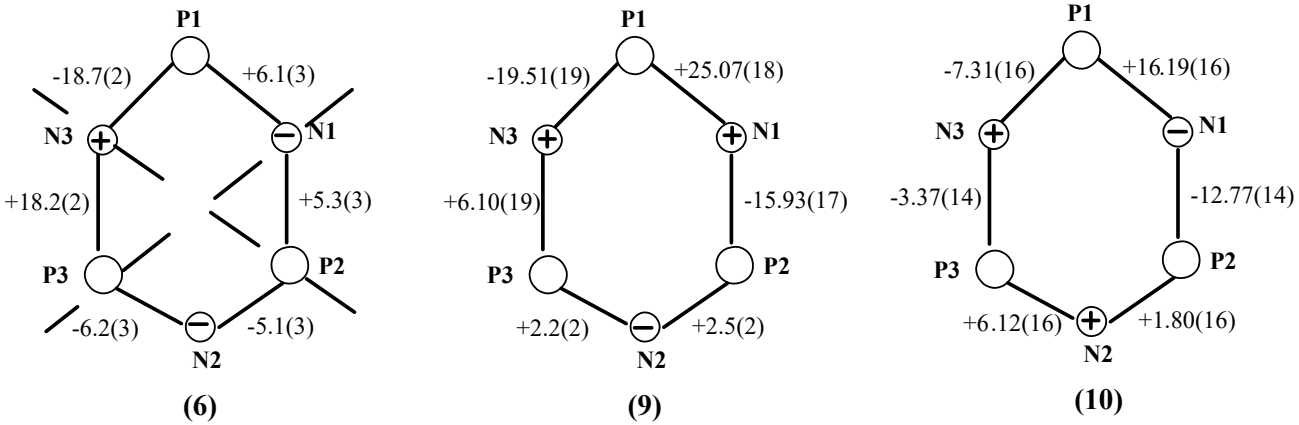


Fig. S5 The shapes of the phosphazene rings in **6**, **9** and **10** with torsion angles (deg).