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Phosphorus-nitrogen compounds (Part 51): the relationship between spectroscopic and crystallographic data of mono- and di-*spiro*cyclophosphazene derivatives with 4-fluoro/nitrophenylmethyl pendant arm/arms

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Abstract: A great wealth of structural information about phosphazenes can be gleaned from the combined spectroscopic and crystallographic data. When data from ^{31}P NMR spectroscopy and X-ray crystallography are put together like pieces in a puzzle, a number of correlations can be obtained for phosphazene derivatives. A systematic study concerning the correlations among the structural parameters (e.g., ^{31}P NMR data, endocyclic/exocyclic NPN bond angles and bond lengths) revealed some characteristics of mono- and di-*spiro*cyclophosphazene derivatives bearing 4-fluoro/nitrophenylmethyl pendant arm/arms. These correlations include the relationship between the δP_{spiro} shifts, the values of electron density transfer parameters Δ(P–N), and the endocyclic and exocyclic NPN bond angles of the cyclophosphazenes. The structural parameters were compared with each other for 19 compounds of 5 different architectural types of cyclophosphazenes with 5- to 7-membered *spiro*-rings.

Key words: *spiro*Cyclophosphazene, 4-fluoro/nitrophenylmethyl pendant arm, ^{31}P NMR, X-ray crystallography, electron density transfer parameter

1. Introduction

Since 1960, the Cl-replacement reactions of hexachlorocyclotriphosphazene (trimer, $N_3P_3Cl_6$) and octachlorocyclotetraphosphazene (tetramer, $N_4P_4Cl_8$) with monodentate [1,2] and bidentate [3] reagents have been extensively studied. The sequential substitution reactions of the Cl-atoms of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with primary and secondary amines led to the formation of the partly and fully substituted organocyclophosphazenes [4]. The condensation reactions of $N_3P_3Cl_6$ with bidentate reagents yield some interesting products; e.g., *spiro*-, *ansa*-, di*spiro*-, tri*spiro*-, *spiro-ansa*-, *spiro-ansa-spiro*, and *spiro-bino-spiro*-cyclotriphosphazenes [5]. In addition to these compounds, tetramer also gives 2,4-*ansa*-, 2,4-di*spiro*-, 2,6-di*spiro*- and tetra*spiro*-cyclotetraphosphazenes with bidentate reagents [6]. The chlorophosphazenes, $N_3P_3Cl_6$ and $N_4P_4Cl_8$, can undergo regio and stereoselective reactions, as well [7]. In recent years, cyclotri and cyclotetraphosphazenes have started to attract much attention due to their potential stereogenic properties, and biological activities such as antibacterial, antifungal and anti-cancer activities [8–12]. Our group has spent many years on designating and synthesizing novel partly substituted cyclotri and cyclotetraphosphazene derivatives with bidentate ligands {dibenzo-diaza-crown ethers [13–17], dibenzo N_2O_n (n=2–4) [18–21] and benzo NO [22–28] donor

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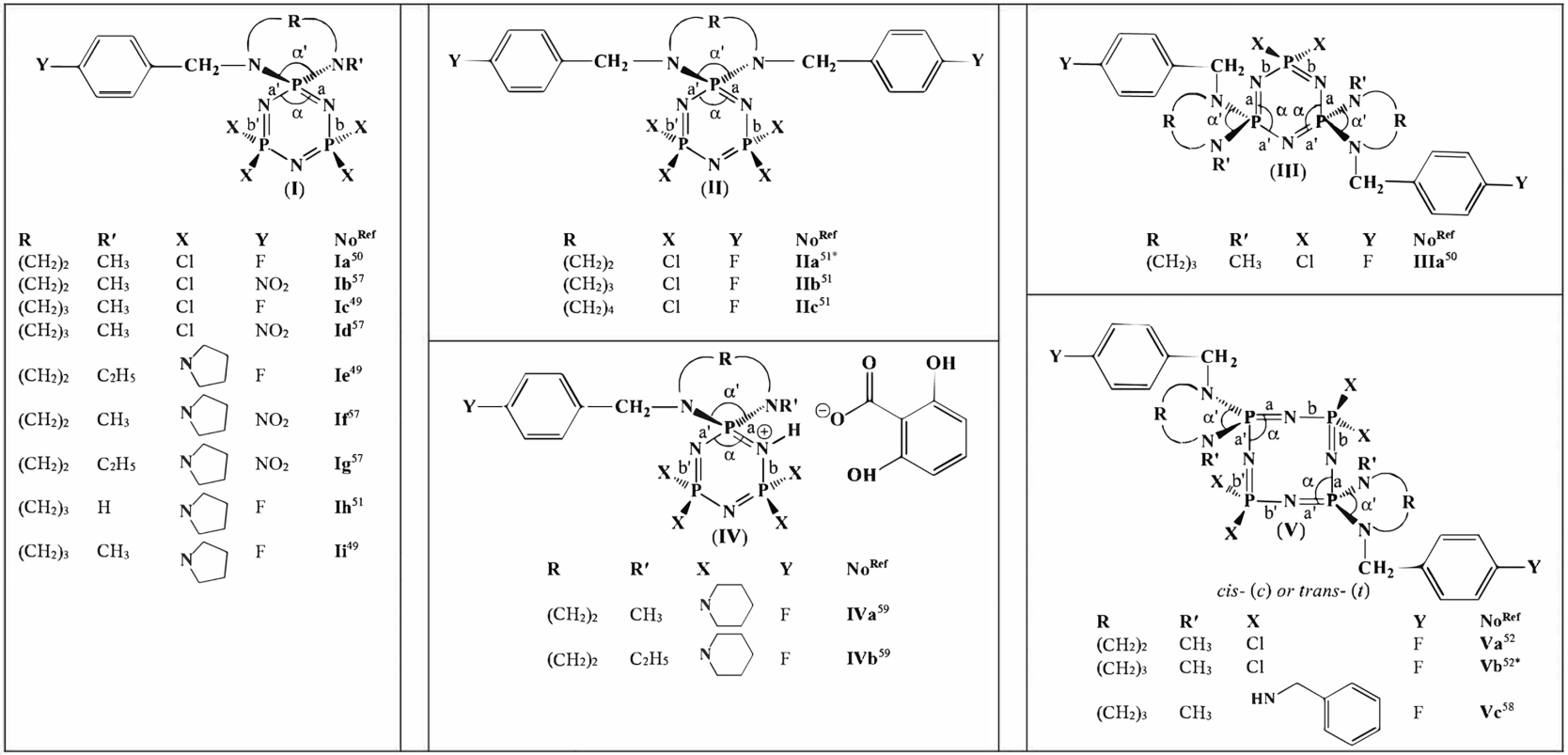
type aminopodands, mono- and bis-ferrocenyldiamines [29–37], sodium (ferrocenylmethylamino)-1-alkoxide [38-43]}and multidentate N_2O_2-donor type dibenzo aminopodands [44–46]. Some interesting phosphazene derivatives such as monotopic and ditopic *spiro*-crypta phosphazenes, *spiro*cyclic phosphaza (PNP-lariat) ethers, cyclophosphazenes possessing 6-membered *spiro* ring/rings, mono and bisferrocenyl*spiro*cyclophosphazenes, and *spiro-ansa-spiro-*, *spiro-bino-spiro-* and *ansa-spiro-ansa*-phosphazenes were synthesized. Besides this, our research group has long focused on performing substituent exchange reactions of Cl–atoms in partly substituted derivatives with heterocyclic amines {pyrrolidine, piperidine, morpholine, 1,4-dioxa-8-azaspiro[4,5]decane, 1-(2-aminoethyl)pyrrolidine, 1-(2-aminoethyl) piperidine, 4-(2-aminoethyl)morpholine}and vanillin side groups, aiming at investigating spectral properties, cytotoxic, antituberculosis and antimicrobial activities, and DNA interactions of the obtained fully substituted cyclophosphazenes. In the last decade, 4-fluorobenzyl pendant armed mono*spiro* and di*spiro* phosphazenes were prepared from the separate reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with 4-fluorobenzyl-NN/NO donor type ligands [47–52]. The phosphezenium salts (protic ionic liquids, PILs or protic molten salts, PMOSs) of fully substituted 4-fluorobenzyl *spiro*cyclotriphosphazenes were also synthesized via reactions of free phosphazene bases with bulky organic acids [53–55]. The spectroscopic and stereogenic properties, and biological activity (antibacterial, antifungal, and cytotoxic activities) of all the (4-fluorobenzyl)*spiro*cyclophosphazenes and some of their phosphazenium salts have been investigated by our research groups [47–55].

Although a large number of papers published by our research group are available on cyclophosphazenes that provide information on their structures, synthesis, and biological activities; the present study focuses on correlation among the structural parameters of mono- and di-*spiro*cyclophosphazene derivatives with 4-fluoro/nitrophenylmethyl pendant arm/arms. In 1986, a systematic study on the relationship between the crystallographic and ^{31}P NMR spectral data on phosphazenes was described for the first time by Shaw [56]. Our group has published many studies on the correlations among the structural parameters of various types of cyclotriphosphazenes bearing structurally analogous motifs. It was found out that in cyclotriphosphazene derivatives, variations in the ^{31}P NMR shifts depend primarily on the electronic, steric and conformational factors (e.g., electron-releasing and withdrawing powers of substituents, the steric hindrance between the exocyclic groups), and on the differences in the bond lengths and bond angles around the phosphorus atoms, particularly endocyclic (α) and on exocyclic (α') bond angles. As a particular interest in our ongoing studies on phosphazene-based chemistry, the present study primarily focuses on a number of correlations established among the structural parameters in mono- and di-*spiro*cyclophosphazene derivatives with 4-fluoro/nitrophenylmethyl pendant arm/arms of the compounds previously synthesized and published by our research group (Table 1) [49–52,57–59]. In this context, here we report our findings on the relationship among the δP_{spiro} shifts with endocyclic and exocyclic NPN bond angles, and electron density transfer parameters, and a brief description of the synthesis methods of 5 types and a total of 19 cyclotri/tetraphosphazenes containing 4-fluoro/nitrophenylmethyl pendant arm and 5- to 7-membered *spiro*-rings.

Table 1. The endocyclic (α) and exocyclic (α') NPN bond angles and bond lengths (a, a ′, b, and b′) on the formulae of cyclophosphazenes.



R	R′	X	Y	No[Ref]
$(CH_2)_2$	CH_3	Cl	F	**Ia**[50]
$(CH_2)_2$	CH_3	Cl	NO_2	**Ib**[57]
$(CH_2)_3$	CH_3	Cl	F	**Ic**[49]
$(CH_2)_3$	CH_3	Cl	NO_2	**Id**[57]
$(CH_2)_2$	C_2H_5	N	F	**Ie**[49]
$(CH_2)_2$	CH_3	N	NO_2	**If**[57]
$(CH_2)_2$	C_2H_5	N	NO_2	**Ig**[57]
$(CH_2)_3$	H	N	F	**Ih**[51]
$(CH_2)_3$	CH_3	N	F	**Ii**[49]

R	X	Y	No[Ref]
$(CH_2)_2$	Cl	F	**IIa**[51*]
$(CH_2)_3$	Cl	F	**IIb**[51]
$(CH_2)_4$	Cl	F	**IIc**[51]

R	R′	X	Y	No[Ref]
$(CH_2)_2$	CH_3	N	F	**IVa**[59]
$(CH_2)_2$	C_2H_5	N	F	**IVb**[59]

R	R′	X	Y	No[Ref]
$(CH_2)_3$	CH_3	Cl	F	**IIIa**[50]

R	R′	X	Y	No[Ref]
$(CH_2)_2$	CH_3	Cl	F	**Va**[52]
$(CH_2)_3$	CH_3	Cl	F	**Vb**[52*]
$(CH_2)_3$	CH_3	HN	F	**Vc**[58]

*The molecules (**IIa** and **Vb**) have a center of symmetry, a=a′ and b=b′ for **IIa**.

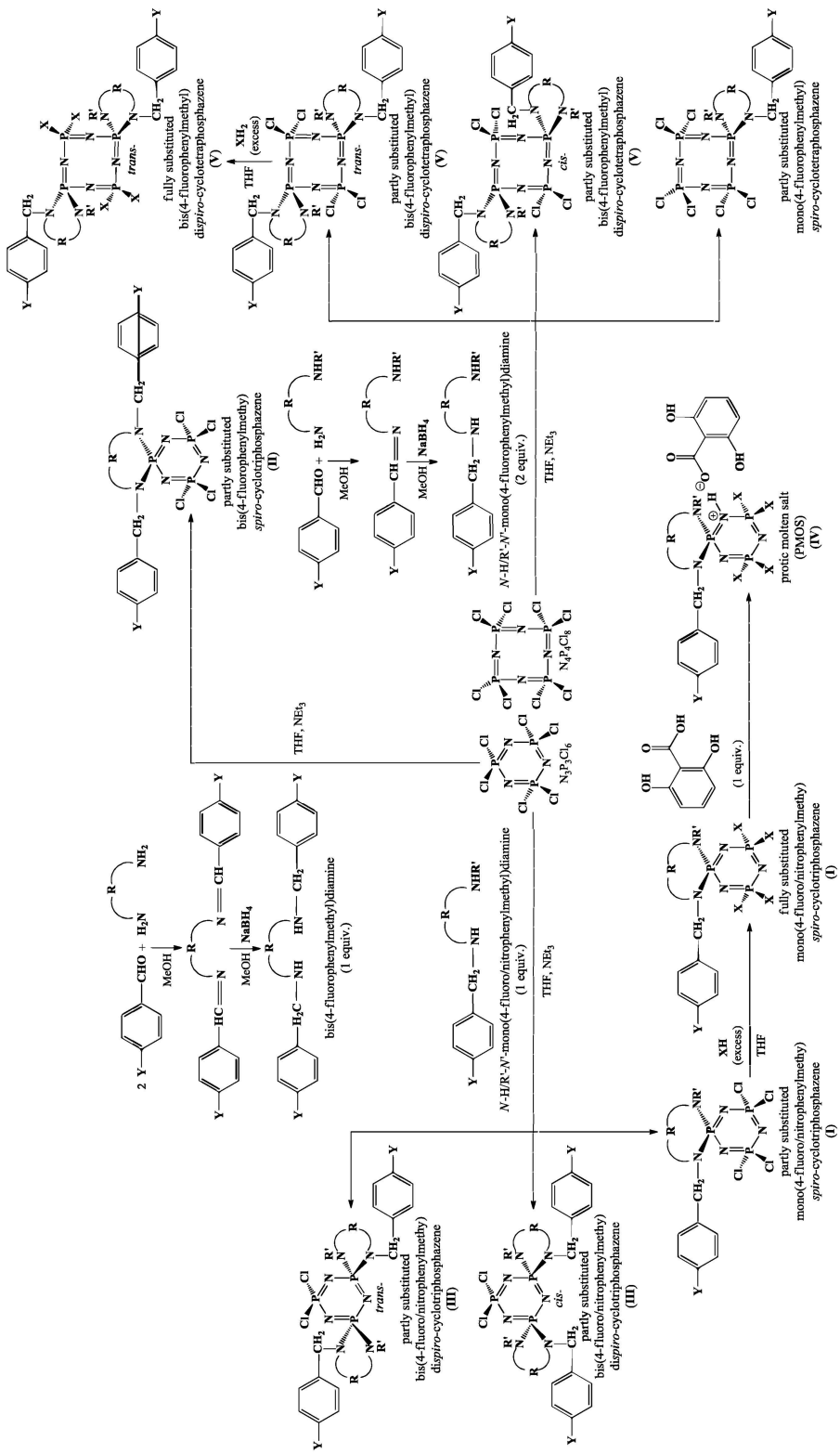
2. Results and discussion

2.1. Synthesis

Routes used for the preparation of mono- and di-*spiro*cyclophosphazene derivatives with 4-fluoro/nitrophenylmethyl pendant arm were given in Scheme. *N*-H-R′-*N*′-mono(4-fluoro/nitrophenylmethyl)diamines [49,57] and bis(4-fluorophenylmethyl)diamines [51] were prepared via reducing the corresponding Schiff bases obtained from the reactions between 4-fluoro/nitrobenzaldehyde and the appropriate *N*-alkyldiamines and *N*,*N*′-bisalkyldiamines in MeOH. The Cl-replacement reactions of $N_3P_3Cl_6$ with 4 equimolar amounts of *N*-H-R′-*N*′-mono(4-fluoro/nitrophenylmethyl)diamines in dry THF at ambient temperature to produce 2 different types of products, namely partly substituted mono(4-fluoro/nitrophenylmethyl)*spiro*cyclotriphosphazenes (**I**) [49,50,57] and *cis*/*trans*-bis(4-fluoro/nitrophenylmethyl)di*spiro*cyclotriphosphazenes (**III**) [50]. The mono*spiro* (**I**) and bisdi *spiro* (**III**) derivatives were separated via column chromatography. Partly substituted bis(4-fluorophenylmethyl) *spiro*cyclotriphosphazenes (**II**) were synthesized by reacting $N_3P_3Cl_6$ with bis(4-fluorophenylmethyl)diamines in dry THF [51]. Fully pyrrolidine substituted phosphazenes (**I**) were prepared by replacing 4 Cl-atoms on the partly substituted derivatives (**I**) with excess pyrrolidine in boiling THF [49,57]. On the other hand, the partly substituted mono(4-fluorophenylmethyl) *spiro*cyclotetraphosphazenes and *cis*/*trans*-bis(4-fluorophenylmethyl)di*spiro*cyclotetraphosphazenes (**V**) were obtained by reacting $N_4P_4Cl_8$ with 2 equimolar amounts of *N*-H-R′-*N*′-mono(4-fluorophenylmethyl)diamines in THF [52]. The 2 different products obtained were separated via column chromatography using toluene. Fully benzylamine substituted bis(4-fluorophenylmethyl) di*spiro*cyclotetraphosphazene was prepared by reacting partly substituted one with excess benzylamine in dry THF at 25 °C [58]. The PMOS (**IV**) derivatives were obtained from the reaction of the corresponding piperidine substituted phosphazenes with gentisic acid in THF [59].

2.2. Correlation among the structural parameters

The endocyclic (α) and exocyclic (α') NPN bond angles, and the bond lengths (a, a′, b, and b′) on the general formulae of cyclotri/tetraphosphazenes containing 4-fluoro/nitrophenylmethyl pendant arm/arms and 5-, 6- and 7-membered *spiro*-ring/rings are given in Table 1. The δP_{spiro} shifts, α and α' bond angles, and Δ(P–N) values are listed in Table 2. The corresponding values for the δP_{spiro} shifts of the standard compounds trimer $N_3P_3Cl_6$ [60,61] and tetramer $N_4P_4Cl_8$ [62,63] were taken from the literature. Type **I** group members are partly and fully substituted mono(4-fluoro/nitrophenylmethyl)*spiro*-cyclotriphosphazenes. The partly substituted bis(4-fluorohenylmethyl) *spiro*- *and* di*spiro*-cyclotriphosphazenes constitute type **II** and **III** compounds, respectively. The phosphezenium salts of fully substituted mono(4-fluorophenylmethyl)*spiro*-cyclotriphosphazenes are members of type **IV**. Members of type **V** are partly and fully substituted *cis*/*trans*-bis(4-fluorophenylmethyl)di*spiro*cyclotetraphosphazenes.



Scheme. Routes for the preparation of mono- and di-*spiro*cyclophosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms investigated in this study.

Table 2. Endocyclic (α) and exocyclic (α') NPN bond angles, bond lengths (a, a′, b, and b′), δP_{spiro} shifts and Δ(P-N) values for the cyclophosphazenes [δP_{spiro} shifts in ppm, α and α' angles in °, a, a′, b, and b′ lengths in Å].

Compound	a	a′	b	b′	Δ(P-N)	α	α'	δP_{NPN}	
Ia[50]	1.607(3)	1.601(3)	1.557(3)	1.555(3)	0.048	111.28(14)	95.46(15)	19.22	for (**I**), (**II**) and (**IV**) and (**V**) $\Delta(P-N) = \frac{a+a'}{2} - \frac{b+b'}{2}$ for (**III**) $\Delta(P-N) = \frac{a+a'}{2} - b$
	1.607(3)	1.600(3)	1.557(3)	1.556(3)	0.047	111.01(15)	94.97(17)		
Ib[57]	1.602(3)	1.614(3)	1.554(3)	1.554(3)	0.054	112.3(1)	95.3(1)	19.35	
Ic[49]	1.630(3)	1.607(3)	1.551(3)	1.558(3)	0.064	111.6(1)	103.9(2)	14.34	
Id[57]	1.627(2)	1.603(2)	1.559(2)	1.566(2)	0.0525	113.6(7)	103.2(6)	14.35	
Ie[49]	1.588(1)	1.590(1)	1.598(1)	1.599(1)	–0.0095	115.1(6)	93.4(5)	27.68	
If[57]	1.594(2)	1.592(2)	1.603(2)	1.601(2)	–0.009	115.3(2)	92.11(2)	27.40	
Ig[57]	1.589(4)	1.585(4)	1.590(4)	1.603(5)	–0.0095	115.0(2)	94.0(2)	27.25	
Ih[51]	1.592(1)	1.592(2)	1.611(1)	1.595(1)	–0.011	118.3(1)	102.4(1)	20.56	
Ii[49]	1.595(1)	1.585(1)	1.598(1)	1.606(1)	–0.012	118.2(6)	101.4(6)	23.44	
IIa[51*]	1.617(0)	1.617(0)	1.563(1)	1.563(1)	0.0535	111.4(2)	94.7(0)	18.00	
IIb[51]	1.631(2)	1.607(2)	1.556(2)	1.560(2)	0.061	111.0(1)	104.2(1)	12.70	
IIc[51]	1.619(1)	1.615(2)	1.559(1)	1.561(1)	0.057	113.2(1)	102.6(1)	16.33	
IIIa[50]	1.607(2)	1.599(3)	1.566(7)	-	0.037	115.71(12)	104.03(13)	19.98	
	1.630(2)	1.576(3)	1.558(3)	-	0.045	113.90(13)	102.75(13)		
IVa[59]	1.651(3)	1.557(3)	1.657(3)	1.607(3)	–0.028	109.86(14)	94.74(14)	13.10	
IVb[59]	1.6541(16)	1.5670(17)	1.6634(17)	1.6071(17)	–0.0247	109.86(9)	94.79(10)	13.01	
***t*-Va**[52]	1.588(2)	-	1.542(2)	-	0.046	112.07(9)	99.12(9)	6.54	
***c*-Vb**[52]	1.584(2)	1.611(2)	1.552(2)	1.545(2)	0.049	114.51(12)	102.63(11)	1.52	
***t*-Vb**[52*]	1.555(2)	-	1.570(2)	-	–0.015	112.34(10)	102.14(10)	1.74	
***t*-Vc**[58]	1.5815(18)	1.5851(18)	1.6027(18)	1.5811(18)	–0.0086	118.06(10)	104.10(11)	6.27	
	1.5827(19)	1.5830(18)	1.5970(19)	1.5759(18)	–0.0036	118.11(10)	103.87(10)		

*The molecules (**IIa** and **Vb**) have a centre of symmetry, a=a′ and b=b′ for **IIa**.

2.2.1. The relationship among the δP_{spiro} shifts and the electron density transfer parameters Δ(P–N)

The electron density transfer parameter Δ(P–N) is the difference between the bond lengths of 2 adjacent endocyclic P-N bonds and is a measure of the electron-releasing and withdrawing powers of the substituents on cyclophosphazene ring. The Δ(P–N) values were calculated using the appropriate equations presented in Table 2 for *spiro*cyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. If electron-withdrawing substituents are bonded to phosphorus atoms, Δ(P–N) values increase. On the other hand, in case of electron-releasing substituents the Δ(P–N) values decrease. The relationship between the δP_{spiro} shifts and the Δ(P–N) values is given in Figure 1 for partly and fully pyrrolidine and benzylamine substituted *spiro*cyclic phosphazenes.

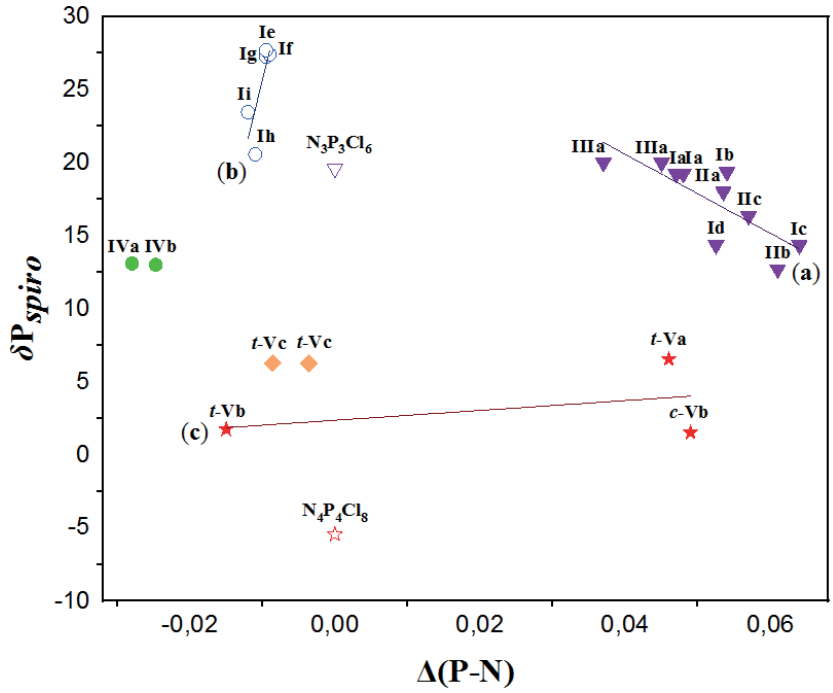


Figure 1. The relationship between δP_{spiro} shifts and Δ(P-N) values for partly and fully pyrrolidine and benzylamine substituted *spiro*cyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. δP_{ClPCl} shift values of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ are 19.60 [61] and –5.45 [63] ppm, respectively.

The linear correlation between δP_{spiro} shifts and Δ(P–N) values observed in 3 groups of cyclophosphazenes are given in Figure 1. When comparing partly substituted types **I**, **II,** and **III** phosphazenes (a) with the fully pyrrolidine substituted type **I** phosphazenes (b), an inverse relation is observed in Figure 1. The Δ(P–N) values could be interpreted by comparing these values with the ones for partly (a) and fully (b) substituted cyclophosphazenes. While fully pyrrolidine substituted cyclotriphosphazenes (**Ie-Ii**) have negative Δ(P–N) values, the partly substituted ones (**Ia-Id**, **IIa-IIc** and **IIIa**) have positive values, and the value of the standard compound $N_3P_3Cl_6$ is zero indicating that the electron-releasing powers of nitrogen atoms in pyrrolidine groups to phosphazene ring is greater than those of the Cl-atoms. Moreover, there is a significant difference between the Δ(P–N) values of *cis*- and *trans*-structures of the same compound of type **V** phosphazenes (c) (0.049 for ***c*-Vb** and -0.015 for ***t*-Vb**). It is possibly due to the different types of hydrogen bond

interactions; e.g., intermolecular C-H—F for ***t*-Vb** and intramolecular C-H—N for ***c*-Vb** [52]. As expected, the Δ(P–N) value of benzylamine substituted ***t*-Vc** is larger than the value of Δ(P–N), which is zero, for the standard compound $N_4P_4Cl_8$.

The Y group (F or NO_2) placed at the *para* position on the benzene ring is an electron-withdrawing substituent and does not cause a significant change in the Δ(P–N) values. However, the points of the NO_2-containing compounds (**Ib** and **Id**) slightly deviate from the linear trend (Figure 1).

Considering the electron-releasing capacity of the 4-fluorophenylmethyl pendant group for type **I-III** partly substituted cyclotriphosphazenes with 6-membered *spiro*-ring, the following order is established: **IIIa** >**IIb** >**Ic**. While the compounds **Ia** and **IIb** are mono- and bis-4-fluorophenylmethyl *spiro*-structures, respectively, compound **IIIa** is bis-4-fluorophenylmethyl di-*spiro* structure. As expected, the electron-releasing strength of 2 4-fluorophenylmethyl pendant groups is more than that of 1 4-fluorophenylmethyl pendant group. However, the same trend is not observed for 5-membered **Ia** and **IIa**. This is due to the fact that **Ia** has 2 independent molecules in the asymmetric unit [50].

There is no significant difference between the Δ(P–N) values of type **II** phosphazenes containing the *spiro*-rings with 6- (**IIb**) and 7- (**IIc**) membered. However, the Δ(P–N) values of the phosphazene with 6-membered *spi*ro-ring (**IIa**) is slightly larger than that of the phosphazene with 5-membered *spiro*-ring (**IIb**). That could be significantly attributed to the fact that 5-membered *spi*ro-ring of **IIa** is in the twisted conformation and 6-membered *spiro*-ring of **IIb** is in the chair conformation [51].

The relationship between Δ(P–N) and δP_{spiro} shifts strongly indicates the basicity of the nitrogen atoms in the phosphazene ring. The basicity of the chlorocyclophosphazene ring containing nitrogen atoms is quite low, and it can be improved by replacing Cl-atoms with electron-releasing substituents on phosphorus. Therefore, the basicity of the nitrogen atoms on the cyclotriphosphazene ring, which is both adjacent (N2-P_{spiro}) and nonadjacent to the *spiro*-ring (N1-PX_2) in fully pyrrolidine substituted cyclotriphosphazenes can be compared with those in partly substituted ones. The basicity of the N1 atom/atoms in fully substituted phosphazenes appear(s) to have increased due to electron-releasing power of the heterocyclic amine groups. However, N_2 atoms in partly substituted phosphazenes decreased due to electron-withdrawing power of the Cl-atoms. Nevertheless, protonation of type **I** heterocyclic amine substituted free cyclotriphosphazene bases with bulky organic acids (gentisic and γ-resorcylic acids) took place on the N2-atom [49] (type **V**) instead of N1-atom [54,55] of the 4-fluorobenzyl*spiro*cyclotriphosphazenes. The H^+ ion may be exchanged between the N1- and N2-atoms of the cyclotriphosphazene ring in the solution at ambient temperature. The ^{31}P NMR spectra recorded at low temperatures and the observed spin-systems in the ^{31}P NMR spectra of the PMOSs may also confirm that the H^+ ion can be displaced between the nitrogen atoms of the phosphazene ring. Although the number of type **V** group members is limited, they could be thought of as reference compounds. It appears that the δP*spiro* shifts and the basicity of the ring decrease after PMOS forms.

The double-bond character of the P-N linkage in the cyclophosphazene derivatives is not fully understood. Negative hyperconjugation and ionic bonding alternatives are exclusive [64]. The natural-bond orbital and topological electron-density analyses of the phosphazenes have proved the crucial role of negative hyperconjugation in description of the P-N bond. An increase in the electron-releasing power of heterocyclic amine substituents seems to cause an increase in the negative hyperconjugation. The electron − withdrawing substituents such as Cl-atom increase the Δ(P–N) values since they attract electrons from *spiro*-ring/rings to the phosphorus atom. However, the electron-releasing substituents such as pyrrolidine group decrease the Δ(P–N) values resulting

in decreased bond lengths (a and a′) and increased bond lengths (b and b′) when the bond lengths of partly substituted derivatives are compared. Hence, the decrease in the length of the endocyclic P–N bonds and in electron charge density on the exocyclic P-N bonds are likely to be a measure of the electron-releasing power of the substituent and the increase in negative hyperconjugation.

2.2.2. The relationship among the δP_{spiro} shifts, endocyclic (α), and exocyclic (α') NPN bond angles

A cluster of points rather than the linear trend were observed among the δP_{spiro} shifts, and endocyclic (α) and exocyclic (α') NPN bond angles. In Figure 2, all types of phosphazene structures were accumulated in 7 regions A, B, C, D, E, F, and G. The points of partly substituted type **I-III** cyclotriphosphazenes, fully pyrrolidine substituted type **I** phosphazenes, and partly substituted type **V** cyclotetraphosphazenes with 5- and 6-membered *spiro*-rings were accumulated in regions (A and B), (C and D), and (F and G), respectively. The points of type **IV** PMOSs with 5-membered *spiro*-ring were accumulated in region E.

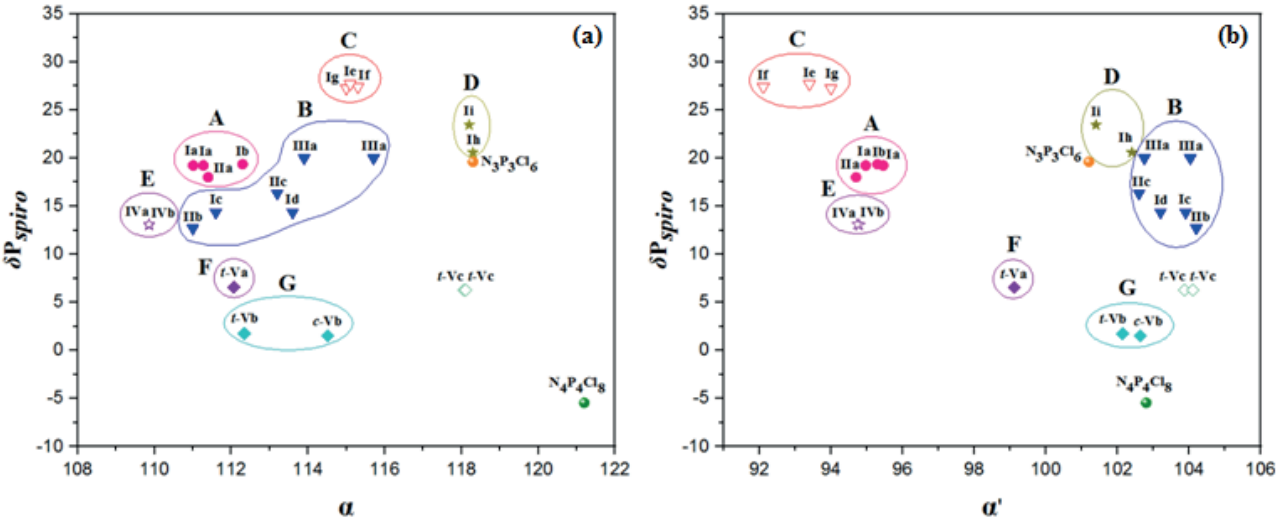


Figure 2. The relationship between $\delta P spiro$ shifts and endocyclic (α) (a) and exocyclic α' (b) NPN bond angles for partly and fully pyrrolidine and benzylamine ubstituted *spiro*cyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. δP_{ClPCl} shift values of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ are 19.60 [61] and -5.45 [63] ppm, respectively. The α and α' values are 118.3(2) and 101.2(1)° for $N_3P_3Cl_6$ [60], 121.2, and 102.8° for $N_4P_4Cl_8$ [62], respectively.

Furthermore, small changes in α and α' bond angles lead to significant changes in δP_{spiro} shifts. A change in the number of members in the *spiro*-ring causes a major change in both α and α' bond angles. In fact, the α and α' bond angles of cyclophosphazenes with 5-membered *spiro*-ring are smaller than those with the 6- and 7-membered ones, and are even smaller than those corresponding to α [118.3(2)°] and α' [101.2(1)°] bond angles [60] in the standard compound, $N_3P_3Cl_6$. Besides, there is a decrease in $\delta P spiro$ shifts with increasing number of members in the *spiro*-ring. For example, the α' bond angles of partly substituted **Ia** with 5-membered *spiro*-ring ($\delta P spiro$ = 19.22 ppm, cycle A) and **Ic** with 6-membered *spiro*-ring ($\delta P spiro$ = 14.34 ppm, cycle B) are respectively; 95.46(15) and 94.97(17), and 103.9(2). This indicates that the electron-releasing power of 5-membered *spiro*-ring to the phosphazene ring is more than that of the 6-membered *spiro*-ring. When partly and fully pyrrolidine substituted type **I** phosphazenes with the same number of members in the *spiro*-ring

(cycles A and C or cycles B and D) are compared, it is seen that the δP*spiro* shifts increase for fully substituted ones. While the α' bond angles decrease, the α bond angles increase. This indicates a change in the substituent groups leading to significant changes in both α and α' bond angles. When considering α bond angles, electrons are transferred from pyrrolidine groups to the cyclotriphosphazene ring in the fully substituted derivatives and from the cyclotriphosphazene ring to Cl-atoms in partly substituted counterparts. When taking into account the α' bond angles, pyrrolidine groups also release electrons to the phosphazene ring, but the Cl-atoms withdraw electrons not only from the phosphazene ring but also from the *spiro*-ring. The elongation of the 2 exocyclic P–N bonds of the *spiro*-ring is likely the best measure of the electron-withdrawing power of the Cl-atoms and the decrease in negative hyperconjugation.

On the other hand, in tetrameric phosphazenes, the α bond angle of fully benzylamine substituted 6-membered phosphazene (**Vc**) is larger with respect to the value of partly substituted counterpart (**Vb**). But, the α' angle of **Vc** is larger than the α' angle of **Vb**. This situation may be attributed to the basicity or electron-releasing power of benzylamine substituent, which is a secondary aliphatic amine group after the substitution, in **Vc** not as high as pyrrolidine substituent, a tertiary heterocyclic amine group after the substitution. When compared α and α' bond angles of type **I** free phosphazene bases (cycle C) and type **IV** PMOSs (cycle E) with 5-membered *spiro*-ring, it is observed that the formation of PMOSs of free phosphazene bases results in a decrease in the α bond angles, and increase in the α' bond angles. In fact, the α' bond angles of PMOSs (**IVa** and **IVb**) are even larger than the corresponding angles in partly substituted cyclotriphosphazenes (cycle A), and the standard compound $N_3P_3Cl_6$, indicating that the positive charge on the N2-atom withdraws electrons from the 5-membered *spiro*-ring in PMOSs.

Besides, the α and α' angles of *cis*- and *trans*-structures of the type **V** cyclotetraphosphazenes with 2 6-membered *spi*ro-rings (***c*-Vb** and ***t*-Vb**) can be compared with each other. The α and α' angles of ***c*-Vb** are considerably and slightly larger than those of ***t*-Vb**, respectively. That could be significantly attributed to the fact that the N_4P_4 ring of *t*-**Vb** has a twisted conformation and the N_4P_4 ring of ***c*-Vb** has a boat conformation [52].

3. Conclusions

The results of a systematic study of *spi*ro-cyclotri/tetraphosphazenes with 4-fluoro/nitrophenylmethyl pendant arm on the basis of correlation between the structural parameters were presented. The main parameters were obtained from X-ray crystallography and ^{31}P NMR results in order to investigate the relationship between the δP_{spiro} shift values and endocyclic and exocyclic NPN bond angles, and electron density transfer parameters. The correlations obtained from the present study ought to be considered as highly informative. Although there are visual comparisons for assessing the accuracy of the relationships, more values are required to learn more about the correlations for cyclophosphazenes. In this approach, our research group or one can plot on the same relationships the new values of the other members of mono- and di-*spiro*cyclophosphazene derivatives bearing 4-fluoro/nitrophenylmethyl pendant arm.

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References

1. Chandrasekhar V, Thilagar P, Pandian BM. Cyclophosphazene-based multi-site coordination ligands. Coordination Chemistry Reviews 2007; 251: 1045-1074.
2. Chandrasekhar V, Chakraborr A. Phosphazenes. In: Allen DW, Loakes D, Tebby JC (editors). Organophosphorus Chemistry. Vol. 48. London, UK: Royal Sciety of Chemistry (RSC) Publishing, 2019, pp. 400-423.
3. Stewart FF. Phosphazenes. In: Allen DW, Loakes D, Tebby JC (editors). Organophosphorus Chemistry. Vol. 44. London, UK: Royal Sciety of Chemistry (RSC) Publishing, 2015, pp. 397-430.
4. Gleria, M, De Jaeger R (editors). Phosphazenes: A Worldwide Insight. New York, NY, USA: Nova Science Publishers, Inc., 2004.
5. Kılıç Z, Okumuş A, Demiriz Ş, Bilge S, Öztürk A et al. Phosphorus-nitrogen compounds: Part 16. Synthesis, stereogenism, anisochronism and the relationship between ^{31}P NMR spectral and crystallographic data of monotopic spiro-crypta phosphazene derivatives. Journal of Inclusion Phenomena and Macrocyclic Chemistry 2009; 65: 269-286.
6. Elmas G, Okumuş A, Koç LY, Soltanzade H, Kılıç Z et al. Phosphorus-nitrogen compounds. Part 29. Syntheses, crystal structures, spectroscopic and stereogenic properties, electrochemical investigations, antituberculosis, antimicrobial and cytotoxic activities and DNA interactions of ansa-spiro-ansa cyclotetraphosphazenes. Europane Journal of Medicinal Chemistry 2014; 87: 662-676.
7. Allen CW. Regio- and stereochemical control in substitution reactions of cyclophosphazenes. Chemical Reviews 1991; 91: 119-135.
8. Başterzi NS, Bilge Koçak S, Okumuş A, Kılıç Z, Hökelek T et al. Syntheses, structural characterization and biological activities of spiro-ansa-spirocyclotriphosphazenes. New Journal of Chemistry 2015; 39: 8825-8839.
9. Machakanur SS, Patil BR, Naik GN, Bakale RP, Bligh SWA et al. Synthesis, characterization and antiproliferative activity of hexa arm starshaped thiosemicarbazones derived from cyclotriphosphazene core. Inorganica Chimica Acta 2014; 421: 459-464.
10. Bhuvan Kumar NN, Kumara Swamy KC. Single diastereomers of unsymmetrical tris-spirocycliccyclotriphosphazenes based on 1,10-bi-2-naphthol-Synthesis and structures. Chirality 2008; 20: 781-789.
11. Uslu A, Yeşilot S. Chiral configurations in cyclophosphazene chemistry. Coordination Chemistry Reviews 2015; 291: 28-67.
12. Elmas G, Okumuş A, Cemaloğlu R, Kılıç Z, Çelik SP et al. Phosphorus-nitrogen compounds. Part 38. Syntheses, characterizations,cytotoxic, antituberculosis and antimicrobial activities and DNA interactions of spirocyclotetraphosphazenes with bis-ferrocenyl pendant arms. Journal of Organometallic Chemistry 2017; 853: 93-106.
13. Bilge S, Demiriz Ş, Okumuş A, Kılıç Z, Tercan B et al. Phosphorus-nitrogen Compounds: Part 13. Syntheses, crystal structures, spectroscopic, stereogenic and anisochronic properties of novel spiro-ansa-spiro-, spiro-bino-spiro- and spiro-crypta phosphazene derivatives. Inorganic Chemistry 2006; 45: 8755-8767.
14. Bilge S, Kılıç Z, Çaylak N, Hökelek T. Phosphorus-nitrogen compounds: Novel *spiro*-crypta-phosphazenes. Structure of {pentane-3-oxa-N,N'-*bis*(1,5-oxybenzyl)-*spiro*(propane-1',3'-diamino)-4,4,6,6-tetrachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene}. Part IX. Journal of Molecular Structure 2004; 707: 139-146.
15. Kılıç Z, Okumuş A, Demiriz Ş, Bilge S, Öztürk A et al. Phosphorus-nitrogen compounds: Part 16. Synthesis, stereogenism, anisochronism and the relationship between ^{31}P NMR spectral and crystallographic data of monotopic *spiro*-crypta phosphazene derivatives. Journal of Inclusion Phenomena and Macrocyclic Chemistry 2009; 65: 269-286.
16. Asmafiliz N, İlter EE, Işıklan M, Kılıç Z, Tercan B et al. Novel phosphazene derivetives. Synthesis, anisochronism and structural investigations of mono- and ditopic *spiro*-crypta phosphazenes. Journal of Molecular Structure 2007; 832: 172-183.

17. Asmafiliz N, İlter EE, Kılıç Z, Hökelek T, Şahin E. Phosphorus-nitrogen compounds: Part 15. Synthesis, anisochronism and the relationship between crystallographic and spectral data of monotopic *spiro*-crypta phosphazenes. Journal of Chemical Sciences 2008; 120: 363-376.

18. Okumuş A, Bilge S, Kılıç Z, Öztürk A, Hökelek T et al. Phosphorus-nitrogen compounds. Part 20: Fully substituted *spiro*-cyclophosphazenic lariat (PNP-pivot) ether derivatives. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2010; 76; 401-409.

19. Özgüç B, Bilge S, Çaylak N, Demiriz Ş, İşler H et al. Phosphorus-nitrogen compounds: Novel *spiro*-cyclophosphazenic lariat (PNP-pivot) ether derivatives. Structures of 4,4,6,6-tetrachloro-2,2-[3-oxa-1,5-pentane dioxy bis(2-phenylamino)cyclo-2λ^5,4λ^5,6λ^5-triphosphazene and 4,4,6,6-tetrachloro-2,2-[1,2-xylylene dioxy bis(2-phenylamino)cyclo-2λ^5, 4λ^5,6λ^5-triphosphazene. Part X. Journal of Molecular Structure 2005; 748: 39-47.

20. Bilge S, Özgüç B, Safran S, Demiriz Ş, İşler H et al. Phosphorus-nitrogen compounds: Novel fully substituted *spiro*-cyclophosphazenic lariat (PNP-pivot) ether derivatives. Structures of 4,4,6,6-tetrapyrrolidino-2,2-[3-oxa-1,5-pentane dioxy bis(2-phenylamino) cyclo-2λ^5,4λ^5,6λ^5-triphosphazene and 4,4,6,6-tetrapyrrolidino-2,2-[1,2-xylylene dioxy bis(2-phenylamino)cyclo[2λ^5,4λ^5,6λ^5]-triphosphazene. Part XI. Journal of Molecular Structure 2005; 748: 101-109.

21. Yıldız M, Kılıç Z, Hökelek T. Phosphorus-nitrogen compounds: Part IV. New podand and lariat ether-type macrocycles with cyclophosphazenes. Structure of 2,2'-[triethyleneglycolbis(phenylether-2-amino)]-2,2',4,4,4',4',6,6,6',6'-decachlorobicyclo-2λ^5, 2'λ^5, 4λ^5, 4'λ^5, 6λ^5, 6'λ^5-triphosphazatriene. Journal of Molecular Structure 1999; 510: 227-235.

22. İlter EE, Çaylak N, Işıklan M, Asmafiliz N, Kılıç Z et al. Phosphorus-nitrogen compounds. *spiro*- and cryptaphosphazene derivatives: Synthesis and spectral investigations. Structure of butane-N,N'-bis(1,4-oxybenzyl)-spiro (propane-1,3-diamino) tetrachloro cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene. Part VII. Journal of Molecular Structure 2004; 697: 119-129.

23. Dal H, Safran S, Süzen Y, Hökelek T, Kılıç Z. Phosphorus-nitrogen compounds: New spiro-cyclic phosphazene derivatives. Structure of 4′, 4′, 6′, 6′-tetrachloro-3,4-dihydro-3-(3-methylpyridin-2-yl) spiro-[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5, 4λ^5, 6λ^5-cyclotriphosphazene)]. Part XII. Journal of Molecular Structure 2005; 753: 84-91.

24. İlter EE, Asmafiliz N, Işıklan M, Kılıç Z, Çaylak N et al. Phosphorus-nitrogen compounds: Part 14. Synthesis, stereogenism and structural investigations of novel N/O *spiro*cyclic phosphazene derivatives. Inorganic Chemistry 2007; 46: 9931-9944.

25. Dal H, Süzen Y. Phosphorus–nitrogen compounds: synthesis and spectral investigations on new *spiro*-cyclic phosphazene derivatives. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2007; 67: 1392-1397.

26. Işıklan M, Asmafiliz N, EE Özalp, İlter EE, Kılıç Z et al. Phosphorus-nitrogen compounds. 21. Syntheses, structural investigations, biological activities, and DNA interactions of new N/O spirocyclic phosphazene derivatives. The NMR behaviors of chiral phosphazenes with stereogenic centers upon the addition of chiral solvating agents. Inorganic Chemistry 2010; 49: 7057-7071.

27. Asmafiliz N, Kılıç Z HayvalıZ, Açık L, Hökelek T et al. Phosphorus-nitrogen compounds. Part 23: Syntheses, structural investigations, biological activities, and DNA interactions of new N/O spirocyclotriphosphazenes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2012; 86: 214-223.

28. Pektaş S, Bilge Koçak S, Başterzi NS, Kılıç Z, Zeyrek CT et al. *spiro*-Cylotriphosphazenes containing 4-hydroxyphenylethyl pendant arm: Syntheses, structural characterization and DNA interaction study. Inorganica Chimica Acta 2018; 474: 51-65.

29. Asmafiliz N, Kılıç Z, Öztürk A, Hökelek T, Koç LY et al. Phosphorus-nitrogen compounds. 18. Syntheses, stereogenic properties, structural and electrochemical investigations, biological activities, and DNA interactions of new spirocyclic mono- and bisferrocenylphosphazene derivatives. Inorganic Chemistry 2009; 48: 10102-10116.

30. Asmafiliz N, Kılıç Z, Öztürk A, Süzen Y, Hökelek T et al. Phosphorus-nitrogen compounds: Part 25. Syntheses, spectroscopic, structural and electrochemical investigations, antimicrobial activities, and DNA interactions of ferrocenyldiaminocyclotriphosphazenes. Phosphorus, Sulfur, and Silicon and the Related Elements 2013; 188: 1723-1742.

31. Asmafiliz N, Kılıç Z, Hökelek T, Koç LY, Açık L et al. Phosphorus-nitrogen compounds: Part 26. Syntheses, spectroscopic and structural investigations, biological and cytotoxic activities, and DNA interactions of mono and bisferrocenylspirocyclotriphosphazenes. Inorganica Chimica Acta 2013; 400: 250-261.

32. Tümer Y, Asmafiliz N, Kılıç Z, Hökelek T, Koç LY et al. Phosphorus-nitrogen compounds: Part 28. Syntheses, structural characterizations, antimicrobial and cytotoxic activities, and DNA interactions of new phosphazenes bearing vanillinato and pendant ferrocenyl groups. Journal of Molecular Structure 2013; 1049: 112-124.

33. Asmafiliz N. Syntheses of chiral phosphazenes with stereogenic centers: NMR behavior in the presence of a chiral solvating agent. Heteroatom Chemistry 2014; 25: 83-94.

34. Okumuş A, Elmas G, Cemaloğlu R, Aydın B, Binici A et al. Phosphorus-nitrogen compounds. Part 35. Syntheses, spectroscopic and electrochemical properties, and antituberculosis, antimicrobial and cytotoxic activities of monoferrocenyl-spirocyclotetraphosphazenes. New Journal of Chemistry 2016; 40: 5588-5603.

35. Elmas G, Okumuş A, Cemaloğlu R, Kılıç Z, Çelik SP et al. Phosphorus-nitrogen compounds. Part 38. Syntheses, characterizations, cytotoxic, antituberculosis and antimicrobial activities and DNA interactions of spirocyclotetraphosphazenes with bis-ferrocenyl pendant arms. Journal of Organometallic Chemistry 2017; 853: 93-106.

36. Tümer Y, Asmafiliz N, Zeyrek CT, Kılıç Z, Açık L et al. Syntheses, spectroscopic and crystallographic characterizations of cis- and trans-dispirocyclic ferrocenylphosphazenes: molecular dockings, cytotoxic and antimicrobial activities. New Journal of Chemistry 2018; 42: 1740-1756.

37. Tümer Y, Asmafiliz N, Arslan G, Kılıç Z, Hökelek T. Phosphorus-nitrogen compounds: Part 45. Vanillinato-substituted cis and trans-bisferrocenyldispirocyclotriphosphazenes: Syntheses, spectroscopic and crystallographic characterizations. Journal of Molecular Structure 2019; 1181: 235-243.

38. Tümer Y, Koç LY, Asmafiliz N, Kılıç Z, Hökelek T et al. Phosphorus-nitrogen compounds: Part 30. Syntheses and structural investigations, antimicrobial and cytotoxic activities and DNA interactions of vanillinato-substituted NN or NO spirocyclic monoferrocenyl cyclotriphosphazenes. Journal of Biological Inorganic Chemistry 2015; 20: 165-178.

39. Asmafiliz N, Civan M, Özben A, Kılıç Z, Ramazanoğlu N et al. Phosphorus-nitrogen compounds. Part 39. Syntheses and Langmuir-Blodgett thin films and antimicrobial activities of N/N and N/O spirocyclotriphosphazenes with monoferrocenyl pendant arm. Applied Organometallic Chemistry 2018; 32(4): e4223.

40. Asmafiliz N, Civan M, Uzunalioğlu N, Özben A, Kılıç Z et al. Phosphorus–nitrogen compounds. Part 41. Ferrocenyl pendant-armed spirocyclopiperidinocyclotriphosphazatrienes: Langmuir–Blodgett thin films and biological activity studies. Journal of Chemical Sciences 2018; 130: 152.

41. İlter EE, Asmafiliz N, Kılıç Z, Açık L, Yavuz M et al. Phosphorus-nitrogen compounds: Part 19. Syntheses, structural and electrochemical investigations, biological activities, and DNA interactions of new spirocyclic monoferrocenylcyclotriphosphazenes. Polyhedron 2010; 29: 2933-2944.

42. Tümer Y, Asmafiliz N, Kılıç Z, Aydın B, Açık L et al. Phosphorus-nitrogen compounds: Part 43. Syntheses, spectroscopic characterizations and antimicrobial activities of cis- and trans-N/O dispirocyclotriphosphazenes containing ferrocenyl pendant arms. Journal of Molecular Structure 2018; 1173: 885-893.

43. Binici A, Okumuş A, Elmas G, Kılıç Z, Ramazanoğlu N et al. Phosphorus-nitrogen compounds. Part 42. The comparative syntheses of 2-cis-4-ansa(N/O) and spiro(N/O) cyclotetraphosphazene derivatives: spectroscopic and crystallographic characterization, antituberculosis and cytotoxic activity studies. New Journal of Chemistry 2019; 43: 6856-6873.
44. Bilge S, Natsagdorj A, Demiriz Ş, Çaylak N, Kılıç Z et al. Phosphorus-nitrogen compounds: Novel spirocyclic phosphazene derivatives. Structure of 3,3"-propane-1,3-diylbis 4',4',6',6'-tetrachloro-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine-2,2'λ^5-[4λ^5,6λ^5] [1,3,5,2,4,6] triazatriphosphorine]]. Helvetica Chimica Acta 2004; 87: 2088-2099.
45. Bilge Koçak S, Koçoğlu S, Okumuş A, Kılıç Z, Öztürk A et al. Syntheses, spectroscopic properties, crystal structures, biological activities, and DNA interactions of heterocyclic amine substituted *spiro-ansa-spiro*- and *spiro-bino-spiro*-phosphazenes. Inorganica Chimica Acta 2013; 406: 160-170.
46. Başterzi, NS, Bilge Koçak S, Okumuş A, Kılıç Z, Hökelek T et al. Syntheses, structural characterization and biological activities of *spiro-ansa-spiro*-cyclotriphosphazenes, New Journal of Chemistry 2015; 39: 8825-8839.
47. Okumuş A, Elmas G, Kılıç Z, Ramazanoğlu N, Açık L et al. The reactions of $N_3P_3Cl_6$ with monodentate and bidentate ligands: The syntheses and structural characterizations, in vitro antimicrobial activities and DNA interactions of 4-fluorobenzyl(N/O)spirocylotriphosphazenes. Turkish Journal of Chemistry 2017; 41: 525-547.
48. Elmas G, Okumuş A, Kılıç Z, Çam M, Açık L et al. Phosphorus-nitrogen compounds. Part 40. The syntheses of (4-fluorobenzyl) pendant armed cyclotetraphosphazene derivatives: Spectroscopic, crystallographic and stereogenic properties, DNA interactions and antimicrobial activities. Inorganica Chimica Acta 2018; 476: 110-122.
49. Akbaş H, Okumuş A, Kılıç Z, Hökelek T, Süzen Y et al. Phosphorus-nitrogen compounds. Part 27. Syntheses, structural characterizations, antimicrobial and cytotoxic activities, and DNA interactions of new phosphazenes bearing secondary amino and pendant (4-fluorobenzyl)spiro groups. European Journal of Medicinal Chemistry 2013; 70: 294-307.
50. Tanrıkulu Gİ, Yakut Özgür M, Okumuş A, Kılıç Z, Hökelek T et al. Phosphorus-nitrogen Compounds. Part 47. The conventional and microwave-assisted syntheses of dispirocyclotriphosphazene derivatives with (4-fluoro/4-nitrobenzyl) pendant arms: Structural and stereogenic properties and DNA interactions. Inorganica Chimica Acta 2019; 490: 179-189.
51. Okumuş A, Kılıç Z, Hökelek T, Dal H, Açık L et al. Phosphorus-nitrogen compounds. Part 22. Syntheses, structural investigations, biological activities and DNA interactions of new mono and bis (4-fluorobenzyl) spirocyclophosphazenes. Polyhedron 2011; 30: 2896-2907.
52. Elmas G, Okumuş A, Sevinç P, Kılıç Z, Açık L et al. Phosphorus-nitrogen compounds. Part 37. Syntheses and structural characterizations, biological activities of mono and bis(4-fluorobenzyl)spirocyclotetraphosphazenes. New Journal of Chemistry 2017; 41: 5818-5835.
53. Akbaş H, Okumuş A, Karadağ A, Kılıç Z, Hökelek T et al. Phosphorus-nitrogen compounds. Part 32. Structural and thermal characterizations, antimicrobial and cytotoxic activities, and in vitro DNA binding of the phosphazenium salts. Journal of Thermal Analysis and Calorimetry 2016; 123: 1627-1641.
54. Elmas G, Okumuş A, Kılıç Z, Gönder LY, Açık L et al. The Syntheses and structural characterizations, antimicrobial activity and in vitro DNA binding of 4-fluorobenzylspıro(N/O)cyclotriphosphazenes and their phosphazenium salts. Journal of the Turkish Chemical Society, Section A: Chemistry 2016; 3: 25-46.
55. Elmas G, Okumuş A, Kılıç Z, Çelik SP, Açık L. The spectroscopic and thermal properties, antibacterial and antifungal Activity and DNA interactions of 4-(fluorobenzyl)spiro(N/O)cyclotriphosphazenium salts. Journal of the Turkish Chemical Society, Section A: Chemistry 2017; 4: 993-1016.
56. Shaw RA. The phosphazenes-structural parameters and their relationships to physical and chemical properties. Phosphorus, Sulfur, and Silicon and the Related Elements 1986; 28: 99-128.

57. Okumuş A, Akbaş H, Kılıç Z, Koç LY, Açık L et al. Phosphorus-nitrogen compounds part 33. In vitro cytotoxic and antimicrobial activities, DNA interactions, syntheses and structural investigations of new mono(4-nitrobenzyl)spirocyclotriphosphazenes. Research on Chemical Intermediates 2016; 42: 4221-4251.

58. Elmas G. The reactions of 2-trans-6-bis(4-fluorobenzyl)spirocyclotetraphosphazene with primary amines: Spectroscopic and crystallographic characterizations. Phosphorus, Sulfur, and Silicon and the Related Elements 2017; 192: 1224-1232.

59. Okumuş A, Akbaş H, Karadağ A, Aydın A, Kılıç Z et al. Antiproliferative effects against A549, Hep3B and FL cell lines of cyclotriphosphazene-based novel protic molten salts: Spectroscopic, crystallographic and thermal results. Chemistry Select 2017; 2: 4988-4999.

60. Bullen GJ. An improved determination of the crystal structure of hexachlorocyclotriphosphazene (phosphonitrilic chloride). Journal of the Chemical Society A: Inorganic, Physical, Theoretical 1971; 56: 1450-1453.

61. Çil E, Arslan M, Görgülü AO. Synthesis and characterization of alkyl- and acyl-substituted oxime-phosphazenes. Canadian Journal of Chemistry 2005; 83: 2039-2045.

62. Wagner AJ, Vos A. The crystal structure of compounds with $(N–P)_n$ rings. IV. The stable modification (T form) of tetrameric phosphonitrilic chloride, $N_4P_4Cl_8$. Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials 1968; 24: 707-713.

63. İbişoğlu H, Çiftçi Yenilmez G, Kılıç A, Tanrıverdi E, Ün İ et al. Formation of novel spiro, spiroansa and dispiroansa derivatives of cyclotetraphosphazene from the reactions of polyfunctional amines with octachlorocyclotetraphosphazatetraene. Journal of Chemical Sciences 2009; 121: 125-135.

64. Chaplin AB, Harrison JA, Dyson PJ. Revisiting the electronic structure of phosphazenes. Inorganic Chemistry 2005; 44: 8407-8417.