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

Aytuğ OKUMUŞ, Gamze ELMAS, Nuran ASMAFİLİZ, Selen BİLGE KOÇAK∗, Zeynel KILIÇ
Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey

Received: 19.11.2019 • Accepted/Published Online: 06.03.2020 • Final Version: .2020

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-spirocyclrophosphazene derivatives bearing 4-fluoro/nitrophenylmethyl pendant arm/arms. These correlations include the relationship between the $\delta P_{spiro}$ shifts, the values of electron density transfer parameters $\Delta(P-N)$, 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: spiroCyclrophosphazene, 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 octachlorocycloketetraphosphazene (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 organocyclrophosphazenes [4]. The condensation reactions of $N_3P_3Cl_6$ with bidentate reagents yield some interesting products; e.g., spiro-, ansa-, dispiro-, trispiro-, spiro-ansa-, spiro-ansa-spiro, and spiro-bino-spiro-cyclotriphosphazenes [5]. In addition to these compounds, tetramer also gives 2,4-ansa-, 2,4-dispiro-, 2,6-dispiro- and tetraspiro-cycloketetraphosphazenes 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 cycloketetraphosphazenes 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

∗Correspondence: sbilge@science.ankara.edu.tr

This work is licensed under a Creative Commons Attribution 4.0 International License.
type aminopodands, mono- and bis-ferrocenyl aminopodands, sodium (ferrocenylmethylamino)-1-alkoxide and multidentate N₂O₂-donor type dibenzo aminopodands. Some interesting phosphazene derivatives such as monotopic and ditopic spiro-crypta phosphazenes, spirocyclic phosphaza (PNP-lariat) ethers, cyclophosphazenes possessing 6-membered spiro ring/rings, mono and bisferrocenylspirocyclophosphazenes, 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 monospiro and dispiro phosphazenes were prepared from the separate reactions of N₃P₃Cl₆ and N₄P₄Cl₈ with 4-fluorobenzyl-NN/NO donor type ligands. The phosphate salts (protic ionic liquids, PILs or protic molten salts, PMOSs) of fully substituted 4-fluorobenzyl spirocyclotriphosphazenes were also synthesized via reactions of free phosphazene bases with bulky organic acids. The spectroscopic and stereogenic properties, and biological activity (antibacterial, antifungal, and cytotoxic activities) of all the (4-fluorobenzyl)spirocyclophosphazenes and some of their phosphazenium salts have been investigated by our research groups.

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 ³¹P NMR spectral data on phosphazenes was described for the first time by Shaw. 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 ³¹P 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). In this context, here we report our findings on the relationship among the δPₚₚᵢᵣₒ 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.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>X</th>
<th>Y</th>
<th>No/Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)</td>
<td></td>
<td>Cl</td>
<td>F</td>
<td>Ia³⁶</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>NO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>Cl</td>
<td>F</td>
<td>Fe⁵⁹</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>NO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>C₆H₅</td>
<td>F</td>
<td>Ie⁸⁹</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>Cl</td>
<td></td>
<td>Hf⁷⁰</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>NO₂</td>
<td></td>
<td>Ig⁵⁵</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>C₆H₅</td>
<td>F</td>
<td>Ih²¹</td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td>C₆H₅</td>
<td>F</td>
<td>Hf⁸⁹</td>
</tr>
</tbody>
</table>

*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-spirocyclonaphosazene 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 N₃P₃Cl₆ 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)spirocyclotriphosphazenes (I) [49,50,57] and cis/trans-bis(4-fluoro/nitrophenylmethyl)dispirocyclotriphosphazenes (III) [50]. The monospiro (I) and bisdi spiro (III) derivatives were separated via column chromatography. Particularly substituted bis(4-fluorophenylmethyl) spirocyclotriphosphazenes (II) were synthesized by reacting N₃P₃Cl₆ 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) spirocyclotetraphosphazenes and cis/trans-bis(4-fluorophenylmethyl)dispirocyclotetraphosphazenes (V) were obtained by reacting N₄P₄Cl₈ 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 dispirocyclotetraphosphazene 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 δPspiro shifts, α and α′ bond angles, and ∆(P-N) values are listed in Table 2. The corresponding values for the δPspiro shifts of the standard compounds trimer N₃P₃Cl₆ [60,61] and tetramer N₄P₄Cl₈ [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-fluorophenylmethyl) spiro- and dispiro-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)dispirocyclotetraphosphazenes.
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 (\(\alpha\)) and exocyclic (\(\alpha'\)) NPN bond angles, bond lengths (a, a', b, and b'), \(\delta\text{P}_{\text{spiro}}\) shifts and \(\Delta(P-N)\) values for the cyclophosphazenes [\(\delta\text{P}_{\text{spiro}}\) shifts in ppm, \(\alpha\) and \(\alpha'\) angles in °, a, a', b, and b' lengths in Å].

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(Å)</th>
<th>a'(Å)</th>
<th>b(Å)</th>
<th>b'(Å)</th>
<th>(\Delta(P-N))</th>
<th>(\alpha)</th>
<th>(\alpha')</th>
<th>(\delta\text{P}_{\text{NPN}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ib (^{57})</td>
<td>1.607(3)</td>
<td>1.607(3)</td>
<td>1.557(3)</td>
<td>1.556(3)</td>
<td>0.048</td>
<td>111.28(14)</td>
<td>95.46(15)</td>
<td>19.22</td>
</tr>
<tr>
<td>Ib (^{57})</td>
<td>1.602(3)</td>
<td>1.600(3)</td>
<td>1.557(3)</td>
<td>1.556(3)</td>
<td>0.047</td>
<td>111.01(15)</td>
<td>94.97(17)</td>
<td>19.35</td>
</tr>
<tr>
<td>Ic (^{49})</td>
<td>1.630(3)</td>
<td>1.607(3)</td>
<td>1.551(3)</td>
<td>1.558(3)</td>
<td>0.064</td>
<td>111.6(1)</td>
<td>103.9(2)</td>
<td>14.34</td>
</tr>
<tr>
<td>Id (^{57})</td>
<td>1.627(2)</td>
<td>1.603(2)</td>
<td>1.559(2)</td>
<td>1.566(2)</td>
<td>0.0525</td>
<td>113.6(7)</td>
<td>103.2(6)</td>
<td>14.35</td>
</tr>
<tr>
<td>Ie (^{49})</td>
<td>1.588(1)</td>
<td>1.590(1)</td>
<td>1.598(1)</td>
<td>1.599(1)</td>
<td>−0.0095</td>
<td>115.1(6)</td>
<td>93.4(5)</td>
<td>27.68</td>
</tr>
<tr>
<td>If (^{57})</td>
<td>1.594(2)</td>
<td>1.592(2)</td>
<td>1.603(2)</td>
<td>1.601(2)</td>
<td>−0.009</td>
<td>115.3(2)</td>
<td>92.11(2)</td>
<td>27.40</td>
</tr>
<tr>
<td>Ig (^{57})</td>
<td>1.589(4)</td>
<td>1.585(4)</td>
<td>1.590(4)</td>
<td>1.603(5)</td>
<td>−0.0095</td>
<td>115.0(2)</td>
<td>94.0(2)</td>
<td>27.25</td>
</tr>
</tbody>
</table>

\(\Delta(P-N) = \frac{a+a'}{2} - \frac{b+b'}{2}\)

for (I), (II) and (IV) and (V)

\(\Delta(P-N) = \frac{a+a'}{2} - b\)

for (III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta(P-N))</th>
<th>(\Delta(P-N))</th>
<th>(\Delta(P-N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ib (^{57})</td>
<td>1.607(3)</td>
<td>1.607(3)</td>
<td>1.557(3)</td>
</tr>
<tr>
<td>Ib (^{57})</td>
<td>1.602(3)</td>
<td>1.600(3)</td>
<td>1.557(3)</td>
</tr>
<tr>
<td>Ic (^{49})</td>
<td>1.630(3)</td>
<td>1.607(3)</td>
<td>1.551(3)</td>
</tr>
<tr>
<td>Id (^{57})</td>
<td>1.627(2)</td>
<td>1.603(2)</td>
<td>1.559(2)</td>
</tr>
<tr>
<td>Ie (^{49})</td>
<td>1.588(1)</td>
<td>1.590(1)</td>
<td>1.598(1)</td>
</tr>
<tr>
<td>If (^{57})</td>
<td>1.594(2)</td>
<td>1.592(2)</td>
<td>1.603(2)</td>
</tr>
<tr>
<td>Ig (^{57})</td>
<td>1.589(4)</td>
<td>1.585(4)</td>
<td>1.590(4)</td>
</tr>
</tbody>
</table>

\*The molecules (IIa and Vb) have a centre of symmetry, a=a' and b=b' for IIa.
2.2.1. The relationship among the $\delta P_{\text{spiro}}$ shifts and the electron density transfer parameters $\Delta (P-N)$

The electron density transfer parameter $\Delta (P-N)$ 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 $\Delta (P-N)$ values were calculated using the appropriate equations presented in Table 2 for spirocyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. If electron-withdrawing substituents are bonded to phosphorus atoms, $\Delta (P-N)$ values increase. On the other hand, in case of electron-releasing substituents the $\Delta (P-N)$ values decrease. The relationship between the $\delta P_{\text{spiro}}$ shifts and the $\Delta (P-N)$ values is given in Figure 1 for partly and fully pyrrolidine and benzylamine substituted spirocyclic phosphazenes.

![Figure 1](image-url)

**Figure 1.** The relationship between $\delta P_{\text{spiro}}$ shifts and $\Delta (P-N)$ values for partly and fully pyrrolidine and benzylamine substituted spirocyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. $\delta P_{\text{ClPCl}}$ 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 $\delta P_{\text{spiro}}$ shifts and $\Delta (P-N)$ 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 $\Delta (P-N)$ 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-IIi) have negative $\Delta (P-N)$ values, the partly substituted ones (Ia-Ic, 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 $\Delta (P-N)$ 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 \( t\text{-}Vb \) and intramolecular C-H—N for \( c\text{-}Vb \) \cite{52}. As expected, the \( \Delta(P-N) \) value of benzyamine substituted \( t\)-\( Vb \) is larger than the value of \( \Delta(P-N) \), which is zero, for the standard compound \( N_4P_4Cl_8 \).

The \( Y \) group (\( F \) or \( NO_2 \)) placed at the \textit{para} position on the benzene ring is an electron-withdrawing substituent and does not cause a significant change in the \( \Delta(P-N) \) 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 \textit{spiro}-ring, the following order is established: \( IIIa > IIb > Ic \). While the compounds \( Ia \) and \( IIb \) are mono- and bis-4-fluorophenylmethyl \textit{spiro}-structures, respectively, compound \( IIIa \) is bis-4-fluorophenylmethyl di-\textit{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 \cite{50}.

There is no significant difference between the \( \Delta(P-N) \) values of type II phosphazenes containing the \textit{spiro}-rings with 6- (\( IIb \)) and 7- (\( IIc \)) membered. However, the \( \Delta(P-N) \) values of the phosphazene with 6-membered \textit{spiro}-ring (\( IIA \)) is slightly larger than that of the phosphazene with 5-membered \textit{spiro}-ring (\( IIb \)). That could be significantly attributed to the fact that 5-membered \textit{spiro}-ring of \( IIa \) is in the twisted conformation and 6-membered \textit{spiro}-ring of \( IIb \) is in the chair conformation \cite{51}.

The relationship between \( \Delta(P-N) \) and \( \delta P_{\text{spiro}} \) 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 \textit{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, \( N2 \) 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 \( \gamma \)-resorcylic acids) took place on the \( N2 \)-atom \cite{49} (type V) instead of \( N1 \)-atom \cite{54,55} of the 4-fluorobenzylspirycyclotriphosphazenes. 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 \( \delta P_{\text{spiro}} \) 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 \cite{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 \( \Delta(P-N) \) values since they attract electrons from \textit{spiro}-ring/rings to the phosphorus atom. However, the electron-releasing substituents such as pyrrolidine group decrease \( \Delta(P-N) \) 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 \(\delta P_{\text{spiro}}\) shifts, endocyclic (\(\alpha\)), and exocyclic (\(\alpha'\)) NPN bond angles

A cluster of points rather than the linear trend were observed among the \(\delta P_{\text{spiro}}\) shifts, and endocyclic (\(\alpha\)) and exocyclic (\(\alpha'\)) 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 \(\text{spiro}\)-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 \(\text{spiro}\)-ring were accumulated in region E.

**Figure 2.** The relationship between \(\delta P_{\text{spiro}}\) shifts and endocyclic (\(\alpha\)) (a) and exocyclic (\(\alpha'\)) (b) NPN bond angles for partly and fully pyrrolidine and benzylamine substituted \(\text{spiro}\)cyclic phosphazenes with 4-fluoro/nitrophenylmethyl pendant arm/arms. \(\delta P_{\text{ClPCl}}\) shift values of \(\text{N}_3\text{P}_3\text{Cl}_6\) and \(\text{N}_4\text{P}_4\text{Cl}_8\) are 19.60 [61] and -5.45 [63] ppm, respectively. The \(\alpha\) and \(\alpha'\) values are 118.3(2) and 101.2(1)° for \(\text{N}_3\text{P}_3\text{Cl}_6\) [60], 121.2, and 102.8° for \(\text{N}_4\text{P}_4\text{Cl}_8\) [62], respectively.

Furthermore, small changes in \(\alpha\) and \(\alpha'\) bond angles lead to significant changes in \(\delta P_{\text{spiro}}\) shifts. A change in the number of members in the \(\text{spiro}\)-ring causes a major change in both \(\alpha\) and \(\alpha'\) bond angles. In fact, the \(\alpha\) and \(\alpha'\) bond angles of cyclophosphazenes with 5-membered \(\text{spiro}\)-ring are smaller than those with the 6- and 7-membered ones, and are even smaller than those corresponding to \(\alpha\) [118.3(2)°] and \(\alpha'\) [101.2(1)°] bond angles [60] in the standard compound, \(\text{N}_3\text{P}_3\text{Cl}_6\). Besides, there is a decrease in \(\delta P_{\text{spiro}}\) shifts with increasing number of members in the \(\text{spiro}\)-ring. For example, the \(\alpha'\) bond angles of partly substituted Ia with 5-membered \(\text{spiro}\)-ring (\(\delta P_{\text{spiro}} = 19.22\) ppm, cycle A) and Ic with 6-membered \(\text{spiro}\)-ring (\(\delta P_{\text{spiro}} = 14.34\) 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 \(\text{spiro}\)-ring to the phosphazene ring is more than that of the 6-membered \(\text{spiro}\)-ring. When partly and fully pyrrolidine substituted type I phosphazenes with the same number of members in the \(\text{spiro}\)-ring
(cycles A and C or cycles B and D) are compared, it is seen that the $\delta P_{\text{spiro}}$ shifts increase for fully substituted ones. While the $\alpha'$ bond angles decrease, the $\alpha$ bond angles increase. This indicates a change in the substituent groups leading to significant changes in both $\alpha$ and $\alpha'$ bond angles. When considering $\alpha$ 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 $\alpha'$ 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 $\text{spiro}$-ring. The elongation of the 2 exocyclic P–N bonds of the $\text{spiro}$-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 $\alpha$ bond angle of fully benzylamine substituted 6-membered phosphazene (Vc) is larger with respect to the value of partly substituted counterpart (Vb). But, the $\alpha'$ angle of Vc is larger than the $\alpha'$ 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 $\alpha$ and $\alpha'$ bond angles of type I free phosphazene bases (cycle C) and type IV PMOSs (cycle E) with 5-membered $\text{spiro}$-ring, it is observed that the formation of PMOSs of free phosphazene bases results in a decrease in the $\alpha$ bond angles, and increase in the $\alpha'$ bond angles. In fact, the $\alpha'$ 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$_3$P$_3$Cl$_6$, indicating that the positive charge on the N2-atom withdraws electrons from the 5-membered $\text{spiro}$-ring in PMOSs.

Besides, the $\alpha$ and $\alpha'$ angles of cis- and trans-structures of the type V cyclotetraphosphazenes with 2 6-membered $\text{spiro}$-rings (c-Vb and t-Vb) can be compared with each other. The $\alpha$ and $\alpha'$ 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$_4$P$_4$ ring of t-Vb has a twisted conformation and the N$_4$P$_4$ ring of c-Vb has a boat conformation [52].

3. Conclusions
The results of a systematic study of $\text{spiro}$-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 $\delta P_{\text{spiro}}$ 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-$\text{spiro}$cyclophosphazene derivatives bearing 4-fluoro/nitrophenylmethyl pendant arm.

Acknowledgments
Selen Bilge Koçak is grateful to the Scientific and Technological Research Council of Turkey (TÜBİTAK) (Project No. 113Z861) and Ankara University Scientific Research Projects (BAP) (Project No. 10B4240008). Zeynel Kılıç thanks Turkish Academy of Sciences (TÜBA) for partial support of this work.
References


19. Öğüz 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-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-triphosphazene} and 4,4,6,6-tetraethylcyclo-2,2-[1,2-xylene dioxy bis(2-phenylamino)cyclo-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-triphosphazene}. Part X. Journal of Molecular Structure 2005; 748: 39-47.

20. Bilge S, Öğüz 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-tetrapyrolidino-2,2-[3-oxa-1,5-pentane dioxy bis(2-phenylamino)cyclo-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-triphosphazene} and 4,4,6,6-tetrapyrolidino-2,2-[1,2-xylene dioxy bis(2-phenylamino)cyclo-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-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\text{'-}[triethyleneglycolbis(phenylether-2-amino)]-2,2\text{'},4,4\text{'},6,6\text{'},6\text{'}-dechlorobicyclo-2\text{\lambda}^5,2\text{'\lambda}^5,4\text{\lambda}^5,4\text{'\lambda}^5,6\text{\lambda}^5,6\text{'\lambda}^5\text{-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 crypta-phosphazene derivatives: Synthesis and spectral investigations. Structure of butane-N,N\text{'}-bis(1,4-oxymethyl)-spiro(propane-1,3-diamino) tetrachloro cyclo-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-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\text{'},4\text{'}\text{'}\text{'}\text{'}-tetrachloro-3,4-dihydro-3-(3-methylpyridin-2-yl) spiro-[1,3,2-benoxazaphosphinine-2,2\text{'\text{'\text{'\text{'}}-2\text{\lambda}^5,4\text{\lambda}^5,6\text{\lambda}^5\text{-cyclophosphazene}]. Part XII. Journal of Molecular Structure 2005; 753: 84-91.


62. Wagner AJ, Vos A. The crystal structure of compounds with \((\text{N–P})_n\) rings. IV. The stable modification (\(T\) form) of tetrameric phosphonitrilic chloride, \(\text{N}_4\text{P}_4\text{Cl}_8\). Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials 1968; 24: 707-713.
