JOTCS A
Journal of the Turkish Chemical Society
Section: A
Chemistry
TURKISH CHEMICAL SOCIETY

Syntheses and Structural Characterizations of First Paraben-Substituted Ferrocenyl Phosphazene Compounds

Yasemin Tümer[1]*, Efsun Şehirli[1], Çiğdem Yüksektepe Ataol[2]

[1]Karabük University, 78050, Karabük, Turkey
[2]Çankırı Karatekin University, 18100, Çankırı, Turkey

Abstract: The Cl replacement reactions of NO (**1**) or NN (**2–5**) spirocyclic monoferrocenyl cyclotriphosphazenes with the potassium salt of ethyl-4-hydroxybenzoate resulted in the full substituted phosphazenes (**6-10**). Their structures have been determined using elemental analysis, FTIR (Fourier transform), ^{1}H (one-dimensional-1D), ^{31}P NMR techniques and X-ray crystallography (for **9** and **10**).

Keywords: Ferrocenylphosphazenes; paraben, ethyl-4-hydroxybenzoate; spectroscopy.

Submitted: .July 11, 2016. **Revised:** November 21, 2016. **Accepted:** November 26, 2016.

Cite this: Tümer Y, Şehirli E, Yüksektepe Ataol Ç. Syntheses and Structural Characterizations of First Paraben-Substituted Ferrocenyl Phosphazene Compounds. JOTCSA. 2017;4(1):299–312.

DOI: To be assigned.

*Corresponding author. E-mail: yasemintumer@karabuk.edu.tr.

INTRODUCTION

The hexachlorocyclotriphosphazene (cyclic trimer, $N_3P_3Cl_6$) is an important compound in the improvement of cyclotriphosphazene derivatives [1], polyorganophosphazenes [2, 3], and phosphazene dendrimers [4, 5]. The phosphorus-nitrogen backbone with six Cl atoms provide an ideal structure for synthesis new cyclotriphosphazene derivatives.

Due to their bactericidal and fungicidal properties, parabens are a class of widely used as preservatives, especially in personal care products, pharmaceuticals, and food [6]. Recently, parabens have been mentioned as a significant substitute group to increase adjuvant [3, 7], water-solubility [3, 8], anti-cancer properties [9] of both the cyclophosphazenes and polyphosphazenes. In addition to that, paraben-substituted polyphosphazene compounds have been considered as hydrogels, membranes [3, 10], and polyelectrolyte materials [11].

In previous studies carried by our group, DNA interactions as well as cytotoxic and antimicrobial activities of ferrocenylphosphazene derivatives were investigated [12, 13, 14]. This study suggests that ferrocenylphosphazenes bearing a paraben derivative (ethyl-4-hydroxybenzoate) could show antimicrobial and cytotoxic activities, and DNA damaging properties. For this purpose, the tetrachloro spirocyclotriphosphazenes with ferrocenyl substituents on the spirocyclic unit (**1-5**) were synthesized as precursor materials which have four active P-Cl bonds [14, 15]. The substitution reactions of **1-5** with ethyl-4-hydroxybenzoate were carried out as emphasized. The structures of the new phosphazene derivatives (**6-10**) (Scheme 1) have been determined using FTIR (Fourier transform), ^{1}H (one-dimensional-1D), ^{31}P NMR techniques and elemental analyses. The molecular and solid-state structures of **9** and **10** were established using single crystal X-ray diffraction methods.

MATERIALS AND METHODS

Reagents

Hexachlorocyclotriphosphazene (Aldrich), ferrocenecarboxaldehyde (Aldrich), ethyl-4-hydroxybenzoate (Aldrich) and aliphatic amines (Fluka) were purchased. These compounds were used without further purification. All solvents we used were dried.

Instruments

The melting points of the new compounds **(6-10)** were determined with a Thermo Scientific apparatus. The ^{1}H NMR spectra were recorded on a Bruker DPX FT-NMR (300

MHz) spectrometer and ^{31}P NMR spectra were recorded on a Bruker Avance III HDNMR (600 MHz) spectrometer. The FTIR spectra were recorded on a Perkin Elmer FTIR (Fourier transform) spectrometer (650-4000 cm^{-1}).

Synthesis of Ferrocenylphosphazene Derivatives

The tetrachloroferrocenylphosphazenes (**1-5**) were synthesized from the reactions of $N_3P_3Cl_6$ with ferrocenylamines according to the methods reported in the literature [14, 15].

1. 4,4',4'',4'''-[(4-Ferrocenyl-1-oxa-4,6,8,10-tetraaza-5λ^5,7λ^5,9λ^5-triphosphaspiro[4.5] deca-5,7,9-triene-7,7,9,9-tetrayl)tetrakis(oxy)]tetrakis(ethyl benzoate) (**6**)

A solution of ethyl-4-hydroxybenzoate (1.24 g, 7.48 mmol) in dry THF (50 mL) was added to a solution of **1** (1.0 g, 1.87 mmol) and potassium carbonate (2.0 g) in dry THF (100 mL) with stirring and refluxing for 72 h. The reaction was followed on TLC silica gel plates using toluene-THF (10:1). After the solvent was evaporated, and the product **(6)** was purified by column chromatography with toluene-THF (10:1) as eluent. (1.54 g, 78 %) Anal. Calcd. for $C_{49}H_{51}FeN_4O_9P_3$: C, 55.90; H, 4.88; N, 5.32. Found: C, 55.89; H, 4.72; N, 5.24. FTIR: 1714 (C=O); 2982, 2930 (C-Haliph.); 1601, 1500, 1475 (C-Carom.); 1094 (C-O); 1265, 1158 (P=N).

2. 4,4',4'',4'''-[(7,11-Diferrocenyl-1,3,5,7,10-pentaaza-2λ^5,4λ^5,6λ^5-triphosphaspiro [4.5] deca-1,3,5-triene-2,4,4,4-tetrayl)tetrakis(oxy)]tetrakis(ethyl benzoate) (**7**)

The same procedure used for 6 was followed for the synthesis of **7**; using **2** (1.0 g, 1.37 mmol), ethyl-4-hydroxybenzoate (0.91 g, 5.47 mmol) and potassium carbonate (2.0 g). (1.44 g, 84%; mp: 154-157 ^oC). Anal. Calcd. for $C_{60}H_{62}Fe_2N_5O_8P_3$: C, 57.66; H, 4.99; N, 5.60. Found: C, 57.34; H, 4.53; N, 6.13. FTIR: 1713 (C=O); 2979, 2918 (C-$H_{aliph.}$); 1600, 1502, 1464 (C-$C_{arom.}$); 1095 (C-O); 1272, 1149 (P=N).

3. 4,4',4'',4'''-[(1-Ferrocenyl-4-methyl-1,4,6,8,10-pentaaza-5λ^5,7λ^5,9λ^5-triphosphaspiro [4.5]deca-5,7,9-triene-7,7,9,9-tetrayl)tetrakis(oxy)]tetrakis(ethyl benzoate) (**8**)

The synthetic route used for **6** was followed for the synthesis of **8**; using **3** (1.0 g, 1.83 mmol), ethyl-4-hydroxybenzoate (1.22 g, 7.31 mmol) and potassium carbonate (2.0 g). (1.37 g, 70%; mp: 182-186 ^oC). Anal. Calcd. for $C_{50}H_{54}FeN_5O_8P_3$: C, 56.30; H, 5.11; N, 6.57. Found: C, 55.75; H, 5.08; N, 6.21. FTIR: 1715 (C=O); 2981 (C-$H_{aliph.}$); 1600, 1503, 1464 (C-$C_{arom.}$); 1095 (C-O); 1265, 1154 (P=N).

4. 4,4',4'',4'''-[(1-Ferrocenyl-4-ethyl-1,4,6,8,10-pentaaza-5λ^5,7λ^5,9λ^5-triphosphaspiro [4.5]deca-5,7,9-triene-7,7,9,9-tetrayl)tetrakis(oxy)]tetrakis(ethyl benzoate) (**9**)

The experimental route used for **6** was followed, using **4** (1.0 g, 1.78 mmol), ethyl-4-hydroxybenzoate (1.19 g, 7.13 mmol) and potassium carbonate (2.0 g). (1.60 g, 83%; mp: 149-152 ^{o}C). The product **9** was dissolved in n-hexane/ THF mixture and crystallized at room temperature. Anal. Calcd. for $C_{51}H_{56}FeN_5O_8P_3$: C, 56.72; H, 5.23; N, 6.48. Found: C, 56.34; H, 5.26; N, 6.34. FTIR: 1715 (C=O); 2980 (C-$H_{aliph.}$); 1599, 1503, 1464 (C-$C_{arom.}$); 1094 (C-O);1258, 1150 (P=N).

5. 4,4',4'',4'''-[(7-Ferrocenyl-11-methyl-1,3,5,7,11-pentaaza-2λ^5,4λ^5,6λ^5-triphosphaspiro [5.5]undeca-1,3,5-triene-2,2,4,4-tetrayl)tetrakis(oxy)]tetrakis(ethyl benzoate) (**10**)
For the synthesis, the same procedure used for **6** was followed; using **5** (1.00 g, 1.78 mmol), ethyl-4-hydroxybenzoate (1.19 g, 7.13 mmol) and potassium carbonate (2.0 g). The product **10** was dissolved in n-hexane/ acetonitrile mixture and crystallized at room temperature. (1.56 g, 81%; mp: 170-172 ^{o}C). Anal. Calcd. for $C_{51}H_{56}FeN_5O_8P_3$: C, 56.72; H, 5.23; N, 6.48. Found: C, 57.22; H, 5.36; N, 6.34. FTIR: 1715 (C=O); 2981 (C-$H_{aliph.}$); 1600, 1503, 1464 (C-$C_{arom.}$); 1094 (C-O);1260, 1158 (P=N).

X-Ray Crystallography

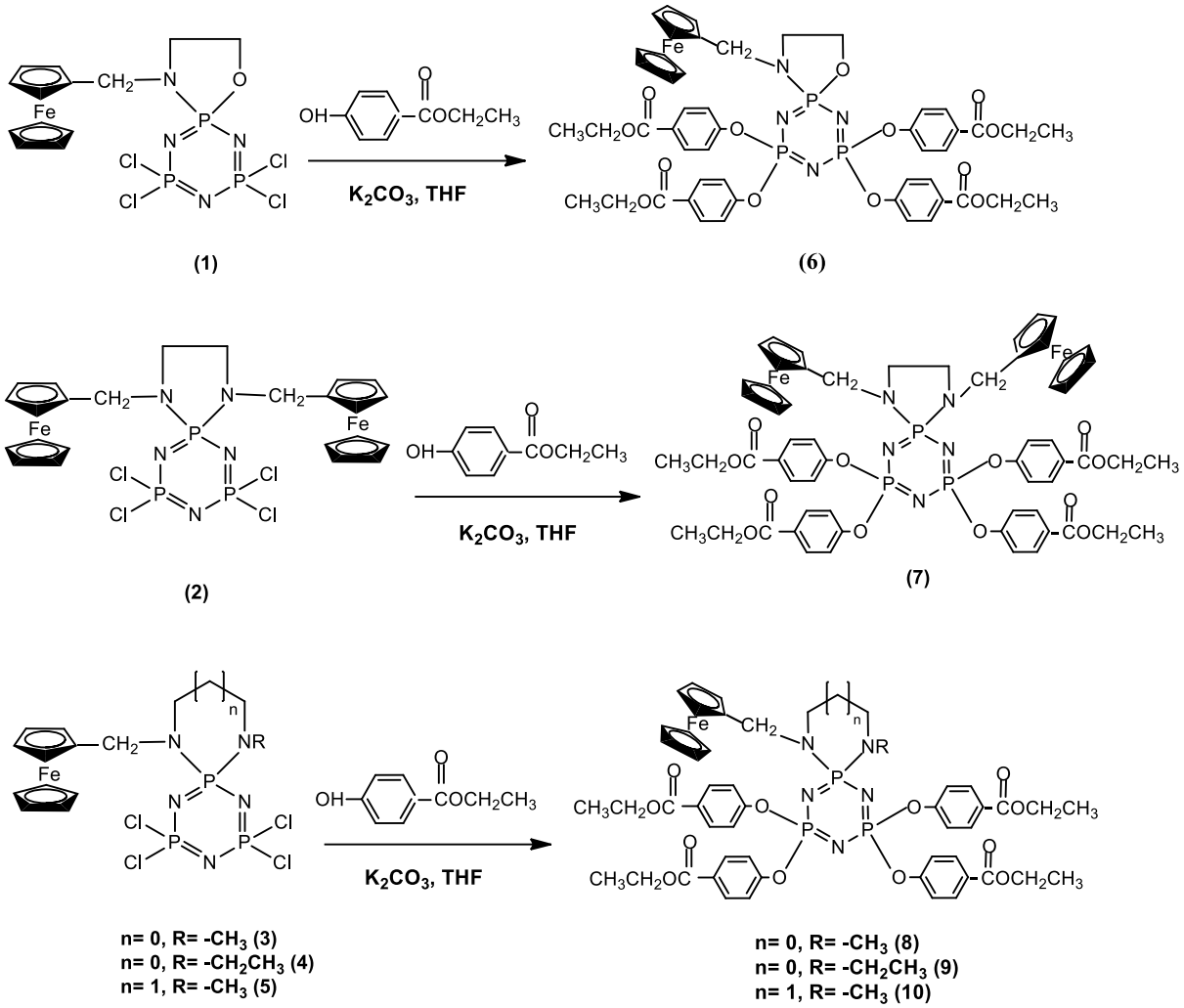
Crystallographic data for **9** and **10** were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo Kα radiation (λ= 0.71073 Å) at T = 296 K. Absorption corrections by multi-scan [21] were applied. Structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data [22]. All non-H atoms were refined anisotropically. Atoms H3A and H3B (for CH_2 group) were placed in a difference synthesis and refined isotropically for **9**. Methyl, aromatic, methine, and methylene H atoms were positioned geometrically at distances of 0.93 (aromatic CH), 0.97 (CH_2), 0.98 (CH) and 0.96 (CH_3) from the parent C atoms; a riding model was used during the refinement process and the Uiso(H) values were constrained to be 1.2 Ueq (for aromatic, methine and methylene carrier atoms) and 1.5 Ueq (for methyl carrier atoms) for **9** and **10**. The principal mean square atomic displacements U of the some of atoms such as C1, C2, C15, C24, C51 and C33 are higher than the other atoms in the compound **10**. According to cif results, this means U values are admitted. The R1 and wR2 indices are obtained higher than expected due to high U displacements of some atoms.

RESULTS AND DISCUSSION

Synthesis and Characterization

The starting compounds (**1-5**) were synthesized in accordance with the published procedure [14, 15]. These precursor compounds have four reactive P-Cl bonds which

may be replaced by the nucleophiles. Utilizing these features tetra-substituted ferrocenylphosphazenes **(6–10)** were obtained from the reactions of **1-5** and potassium salt of ethyl-4-hydroxybenzoate in refluxing THF (Scheme 1). The new compounds in all the reactions were isolated by column chromatography.



Scheme 1. The synthetic route for new phosphazene derivatives **(6-10)**.

The ^{1}H-decoupled ^{31}P NMR spectral data of **6-10** are listed in Table 1. The spin systems of the new compounds are interpreted as AX_2. Compounds **6-10** demonstrate a typical five-line resonance pattern, including a doublet for two substituted P atoms and a triplet for other P(spiro) atom.

The assignments of the ^{1}H NMR signals of the new ferrocenylphosphazene derivatives were made based on the chemical shifts, multiplicities, and coupling constants (Tables S1 and S2). The $FcCH_2N$ protons of paraben-substituted ferrocenylphosphazenes yield the doublets due to the vicinal coupling with the P-31 nucleus, indicating that both geminal

protons are equivalent. The $^{3}J_{PH}$ values of $FcCH_2N$ protons are in the range of 2.63-3.40 Hz. As expected, the nine protons belonging to the ferrocenyl groups are observed as a singlet (3.84-3.98 ppm).

Table 1. The ^{31}P NMR spectral data of **6-10**. [*J* values in Hz and chemical shifts (δ) are reported in ppm]. ^{31}P NMR measurements in $CDCl_3$ solutions at 293 K.

	δ(ppm)			O
Compound	**$P(NO)_{(spiro)}$**	**$P(NNR)_{(spiro)}$**	**$P(OAr)_2$**	**$^{2}J_{PP}$ (Hz)**
6	29.74 (t)	-	10.50 (d)	62.65
7	-	24.97 (t)	10.84 (d)	54.57
8	-	26.33 (t)	10.96 (d)	54.57
9	-	24.46 (t)	10.92 (d)	54.57
10	-	23.07 (t)	9.33 (d)	50.53

The spin system of all compounds is AX_2.

X-ray Structural Studies

The molecular structures of **9** and **10** are shown in Figures 1 and 2. The molecules are comprised of a cyclotriphosphazene core, a spirocyclic diamine with a ferrocenyl substituent, and four terminal ethylbenzoate groups.

The crystals are monoclinic, space groups $P2_1/c$, with *a* = 14.0306(12)Å and 14.3409(13)Å, *b* = 10.9976(8)Å and 10.9552(11)Å, *c* = 33.420(3)Å and 33.0730(32)Å, α, γ = 90° and 90°, β =94.212(3)° and 92.074(3)°, V = 5142.8(7) Å3 and 5192.6(9) Å3, and Z = 4 for **9** and **10**, respectively (Table S3). The phosphazene rings are not planar for **9** and **10**, with a total puckering parameter (Q_T) of 0.126(3)Å and 0.086(4)Å. The conformation of the phosphazene rings of **9** and **10** are twisted-boat [q_2= 0.045(3)Å and 0.033(4)Å, q_3=0.118(3)Å and -0.080(4)Å, Φ_2= 273(4)° and 85(6)° and θ_2= 21.0(14)° and 158(3)°, respectively]. The selected geometric parameters are listed in Table 2. The average endocyclic P−N bond lengths in phosphazene rings [1.636(4) Å for **9** and 1.651(5) Å for **10**] are shorter than the average exocyclic P−N bonds [1.633(4) Å for 9 and 1.643(5) Å for **10**]. There are regular variations with the distances from P1: P3−N2 ≈ P3−N3> P2−N1≈ P1−N1> P1−N2 ≈ P2−N3, P2−N1 ≈ P2−N2> P1−N3≈ P3−N3> P3−N2 ≈ P1−N1 for **9** and **10**, respectively. In the phosphazene rings, the endocyclic (α*)* and exocyclic (α^1) angles of **9** and **10** deviate slightly from those found in the standard compound $N_3P_3Cl_6$ [α 118.3(2)° and $\alpha^1$101.2(1)°] [17-19].

Table 2. Selected bond lenghts (Å) and angles (º) for **9** (α) and **10** (α^1)

Compound 9		**Compound 10**	
P(1)–N(1)	1.575(3)	P(1)–N(1)	1.556(5)
P(1)–N(2)	1.563(3)	P(1)–N(3)	1.588(4)
P(2)–N(1)	1.576(3)	P(2)–N(1)	1.611(5)
P(2)–N(3)	1.557(4)	P(2)–N(2)	1.600(5)
P(3)–N(2)	1.603(4)	P(3)–N(2)	1.566(5)
P(3)–N(3)	1.592(4)	P(3)–N(3)	1.577(5)
P(1)–O(6)	1.587(3)	P(1)–O(1)	1.604(4)
P(1)–O(7)	1.585(3)	P(1)–O(2)	1.605(4)
P(2)–O(1)	1.596(3)	P(3)–O(3)	1.594(4)
P(2)–O(4)	1.599(3)	P(3)–O(4)	1.594(4)
P(3)–N(4)	1.636(4)	P(2)–N(4)	1.651(5)
P(3)–N(5)	1.633(4)	P(2)–N(5)	1.643(5)
N(1)–P(1)–N(2)	118.23(2)	N(1)–P(1)–N(3)	118.8(3)
P(1)–N(1)–P(2)	119.80(2)	P(1)–N(3)–P(3)	119.9(3)
N(1)–P(2)–N(3)	118.47(2)	N(3)–P(3)–N(2)	118.8(3)
P(2)–N(3)–P(3)	124.90(2)	P(3)–N(2)–P(2)	123.7(3)
N(3)–P(3)–N(2)	111.99(2)	N(2)–P(2)–N(1)	113.9(3)
P(3)–N(2)–P(1)	124.30(2)	P(2)–N(1)–P(1)	123.9(3)
O(6)–P(1)–O(7)	98.07(2)	O(1)–P(1)–O(2)	97.0(2)
O(1)–P(2)–O(4)	97.71(1)	O(3)–P(3)–O(4)	97.9(2)
N(4)–P(3)–N(5)	94.25(2)	N(4)–P(2)–N(5)	102.7(3)

Full cif depositions, excluding structure factor amplitudes, are lodged with the Cambridge Crystallographic Data Centre, CCDC 1446475 for **9** and CCDC 1451311 for 10. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

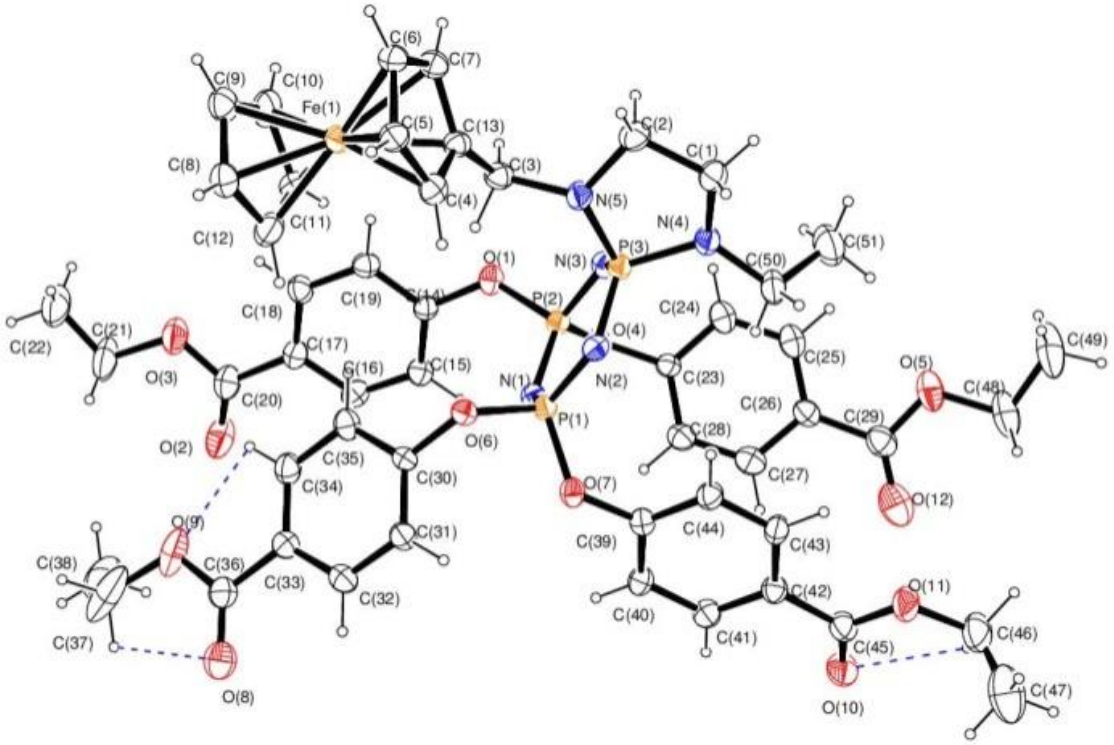


Figure 1. ORTEP-3 [16] drawing of **9** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level.

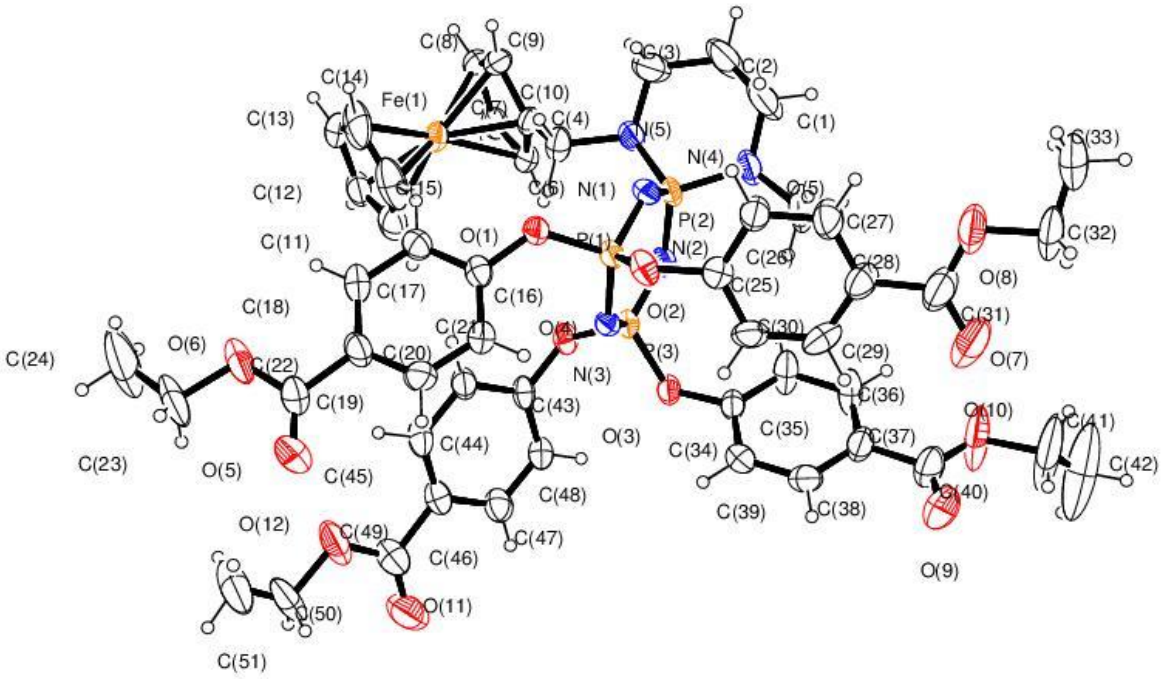


Figure 2. ORTEP-3 [16] drawing of **10** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level.

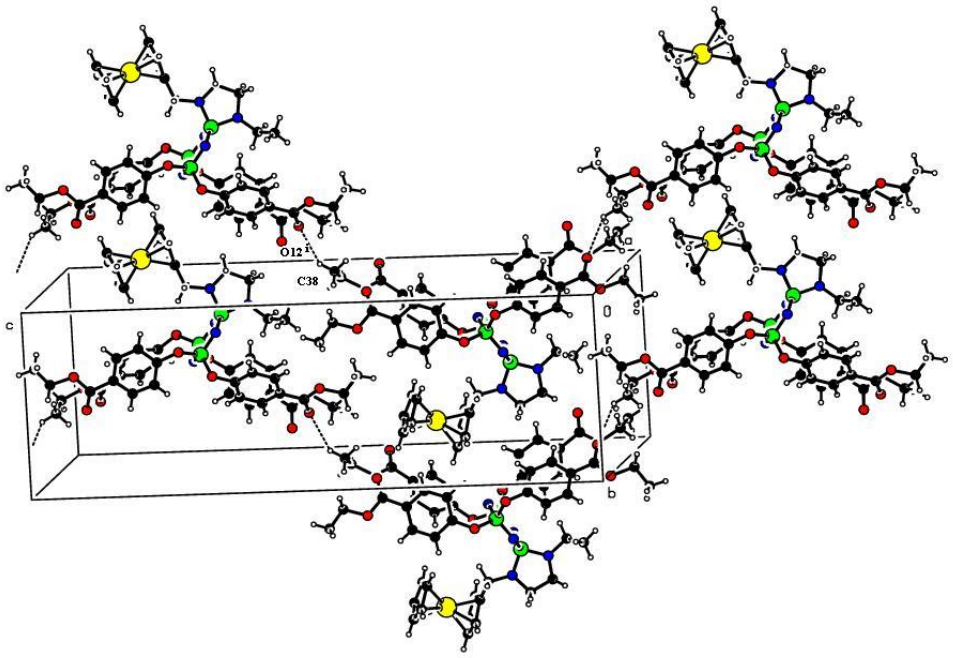


Figure 3. PLUTON [20] drawing of **9** with intermolecular C(38)−H(38A)…O(12)^{I} hydrogen bonding extending along *c* axis. Code of symmetry: (i) x,-1/2-y,1/2+z.

Compound **9** has intermolecular and intramolecular C−H…O hydrogen bonds; however, the hydrogen bonds are found in the compound **10**, which has intramolecular hydrogen bonds. The details of the intramolecular bonds are indicated in Table 3. Also, intramolecular C−H…O interactions can be seen in Figure 1. As seen in Figure 3, these intermolecular hydrogen bonds firstly link the molecules into centrosymmetric dimers, and then these dimers are linked to zig-zag form infinite chains running nearly along the c-axis. On the other hand, the *π* … *π* contact between the ferrocene rings, Cg(2)–Cg(3) [where Cg(2) and Cg(3) are the centroids of the rings (C4–C7/C13) and (C8–C12)] with the centroid–centroid distance of 3.286(3) Å and the C–H…*π* interaction may be effective in the stabilization of the crystal packing (Table 3 and Figure S1).

Table 3. Hydrogen-bond geometry (Å, °) of **9** and **10**. Symmetry codes: (i) x,-1/2-y,1/2+z; (ii) x, 1+y, z.

Compounds	Hydrogen bond(Å,°)	D–H	H...A	D...A	D–H...A
9	C(34)–H(34)...O(9)	0.93	2.38	2.703(7)	100
	C(37)–H(37A)...O(8)	0.97	2.23	2.657(12)	106
	C(46)–H(46A)...O(10)	0.97	2.29	2.663(8)	102
	C(38)–H(38A)...O(12)^{i}	0.96	2.60	3.402(12)	142
	C(6)–H(6)...Cg(7)^{ii}	0.93	2.93	3.698(5)	140
10	C(27)–H(27)...O(8)	0.93	2.40	2.715(10)	100
	C(41)–H(41B)...O(9)	0.97	2.14	2.590(20)	107
	C(45)–H(45)...O(12)	0.93	2.38	2.705(10)	100

CONCLUSIONS

In the current study, paraben-substituted ferrocenylphosphazene derivatives were synthesized. The structures of **9** and **10** were determined using X-ray crystallography. The compounds synthesized are the precursor molecules for further investigations by our research group.

ACKNOWLEDGMENT

The authors acknowledge the "Karabuk University, Scientific Research Unit" (GrantNo. YL20/2014-2) for the financial support and Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

REFERENCES

1. Gleria M, Jaeger RD, editors. Applicative aspects of cyclophosphazenes. New York: Nova Science Publishers; 2004. 371 s. ISBN: 1-59454-026-8.

2. Allcock HR. Chemistry and applications of polyphosphazenes. Hoboken, N.J: Wiley-Interscience; 2003. 725 s. ISBN: 978-0-471-44371-1.

3. Andrianov AK, editor. Polyphosphazenes for biomedical applications. Hoboken, N.J: Wiley; 2009. 462 s. ISBN: 978-0-470-19343-3.

4. Tümer Y, Yüksektepe Ç, Batı H, Çalışkan N, Büyükgüngör O. Preparation and characterization of Hexakis[2-methoxy-4-(2,3-dimethylphenylimino)phenylato]cyclotriphosphazene. Phosphorus, Sulfur, and Silicon and the Related Elements. November 23 2010;185(12):2449–54. DOI: 10.1080/10426501003692078.

5. Çoşut B, Yeşilot S, Durmuş M, Kılıç A. Synthesıs and fluorescence propertıes of hexamerıc and octamerıc subphthalocyanınes based cyclic phosphazenes. Dyes And Pıgments. September 2013;98(3):442–9. DOI: 10.1016/j.dyepig.2013.03.028.

6. Bledzka D, Gromadzinska J, Wasowicz W. Parabens. From environmental studies to human health. Environ. Int., February 2014; 67: 27–42. DOI: 10.1016/j.envint.2014.02.007.

7. Andrianov AK, DeCollibus DP, Gills HA, Kha HH, Marin A, Prausnitz MR, Babiuk LA, Townsend H, Mutwiri G. Poly[di(carboxylatophenoxy)phosphazene] is a potent adjuvant for intradermal immunization. P Natl Acad Scı Usa. November 2009; 106 (45): 18936–18941. DOI: 10.1073/pnas.0908842106.

8. Stone ML, Wilson AD, Harrup MK, Stewart FF. An initial study of hexavalent phosphazene salts as draw solutes in forward osmosis. Desalination. March 2013; 312: 130–136. DOI: 10.1016/j.desal.2012.09.030.

9. Çiftçi GY, Şenkuytu E, İncir SE, Yuksel F, Ölçer Z, Yıldırım T, Kılıç A, Uludağ Y. First paraben substituted cyclotetraphosphazene compounds and DNA interaction analysis with a new automated biosensor. Biosensors and Bioelectronics. June 2016; 80: 331-338. DOI: 10.1016/j.bios.2016.01.061.

10. Allcock HR, Kwon S. An ionıcally cross-lınkable polyphosphazene: poly(bıs(carboxylatophenoxy)phosphazene) and its hydrogels and membranes. Macromolecules. February 1989; 22 (1): 75–79. DOI: 10.1021/ma00191a015.

11. Akgol Y, Hofmann C, Karatas Y, Cramer C, Wiemhofer HD, Schönhoff M. Conductivity spectra of polyphosphazene-based polyelectrolyte multilayers. J. Phys. Chem. B. May 2007; 111: 8532-8539. DOI: 10.1021/jp068872w.

12. Asmafiliz N, Kılıç Z, Hökelek T, Açık L, Koç LY, Süzen Y, Öner Y. Phosphorus–nitrogen compounds: Part 26. Syntheses, spectroscopic and structural investigations, biological and cytotoxic activities, and DNA interactions of mono and bisferrocenylspirocyclotriphosphazenes. Inorg. Chim. Acta. May 2013; 400: 250-261. DOI: 10.1016/j.ica.2013.03.001.

13. Tumer Y, Asmafiliz N, Kılıc Z, Hokelek T, Koc LY, Acık L, Yola ML, Solak AO, Oner Y, Dundar D, Yavuz M. 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. October 2013; 1049: 112–124. DOI: 10.1016/j.molstruc.2013.06.036.

14. Tumer Y, Koc LY, Asmafiliz N, Kılıc Z, Hokelek T, Soltanzade H, Acık L, Yola ML, Solak AO. 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. J Biol Inorg Chem. January 2015; 20: 165–178. DOI:10.1007/s00775-014-1223-5.

15. Ilter EE, Asmafiliz N, Kılıc Z, Acık L, Yavuz M, Bali EB, Solak AO, Buyukkaya F, Dal H, Hokelek T. Phosphorus–nitrogen compounds: Part 19. Syntheses, Structural and Electrochemical Investigations, Biological Activities and DNA Interactions of New Spirocyclic monoferrocenylcyclotriphosphazenes. Polyhedron. July 2010; 29: 2933-2944. DOI: 10.1016/j.poly.2010.07.017.

16. Farrugia LJ, ORTEP-3 for Windows- a version of ORTEP-III with a Graphical User Interface (GUI). J Appl. Cryst. 1997; 30; 565. DOI: 10.1107/S0021889897003117.

17. Tumer Y, Batı H, Çalışkan N, Yüksektepe Ç, Büyükgüngör O. Synthesis, Crystal Structure and Characterization of Hexakis[2-methoxy-4-formylphenoxy]cyclotriphosphazene. Z. Anorg. Allg. Chem. March 2008; 634(3): 597–599. DOI: 10.1002/zaac.200700389.

18. Kiliç A, Begeç S, Çetinkaya B, Kiliç Z, Hökelek T, Gündüz N, Yildiz M. Unusual products in the reactions of hexachlorocyclotriphosphazatriene with sodium aryloxides. Heteroatom Chem.December 1996; 7: 249-256. DOI: 10.1002/(SICI)1098-1071(199608)7:4<249::AID-HC6>3.0.CO;2-0.

19. Bullen GJ. An improved determination of the crystal structure of hexachlorocyclotriphosphazene (phosphonitrilic chloride). J. Chem. Soc. A. 1971; 1450-1453. DOI: 10.1039/J19710001450.

20. Spek AL, Acta Cryst., 1990; A 46, C34. PLATON, An Integrated Tool for the Analysis of the Results of a Single Crystal Structure Determination URL: http://journals.iucr.org/a/issues/1990/s1/00/a29681/a29681.pdf

21. Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.

22. Sheldrick GM. A short history of SHELX. Acta Crystallogr. Sect. A. January 2008; 64: 112–122. DOI: 10.1107/S0108767307043930.

İlk Paraben Sübstitüe Ferrosenil Fosfazen Bileşiğinin Sentezi ve Yapısal Karakterizasyonu

Yasemin Tümer, Efsun Şehirli, Çiğdem Yüksektepe Ataol

Öz: Etil 4-hidroksibenzoatın potasyum tuzu ile Cl yerdeğiştirme tepkimesi NO (**1**) veya NN (**2-5**) spirosiklik monoferrosenil siklotrifosfazenlerin (**6-10**) oluşumu ile sonuçlanmıştır. Elde edilen maddelerin yapıları elemental analiz, FTIR (Fourier dönüşüm kızılötesi spektroskopisi), ^{1}H (tek boyutlu 1D), ^{31}P NMR teknikleri ve X-ışını kristalografisi (**9** ve **10**) ile aydınlatılmıştır.

Anahtar kelimeler: Ferrosenilfosfazenler; paraben, etil 4-hidroksibenzoat; spektroskopi.

Sunulma: .11 Temmuz 2016. **Düzeltme:** 21 Kasım 2016. **Kabul:** 26 Kasım 2016.