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# Synthesis of New Derivatives of Cyclotriphosphazene Substituted with the Salen Side Groups

A. Tarassoli* and B. Nekoeishahraki
*Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran*

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The reaction between hexachlorocyclotriphosphazenes ($N_3P_3Cl_6$) and three equivalents of bis-salicylidene ethylene diamine ($HOC_6H_4$-CH=N-$CH_2$-)$_2$ (salen) was investigated in two different experimental conditions. In the presence of anhydrous $Na_2CO_3$ in stirring tetrahydrofuran (THF) medium, the reaction led to a 50:50 mixture of tris[bis(salicylidene)ethylenediamine] cyclotriphosphazene, *spiro*-$N_3P_3$[($OC_6H_4$-CH=N-$CH_2$-)$_2$]$_3$ (**1**) and *ansa* (**2**) fully substituted products, whereas, in toluene solution, $N_3P_3Cl_6$ with salen (**3**) and $Al_2O_3$/KOH afforded the *spiro* (**1**), as the only isolable compound. The spectroscopic data revealed that the oxygen atoms of salen moieties were selectively bonded to the three phosphorus atoms of the phosphazene ring. The new derivatives of cyclotriphosphazenes were characterized by IR spectrophotometry $^1$H NMR, $^{31}$P NMR spectral data and elemental analysis.

**Keywords:** *Ansa*-derivatives, Cyclotriphosphazene, Salen, *Spiro*-derivatives, Supramolecules

## INTRODUCTION

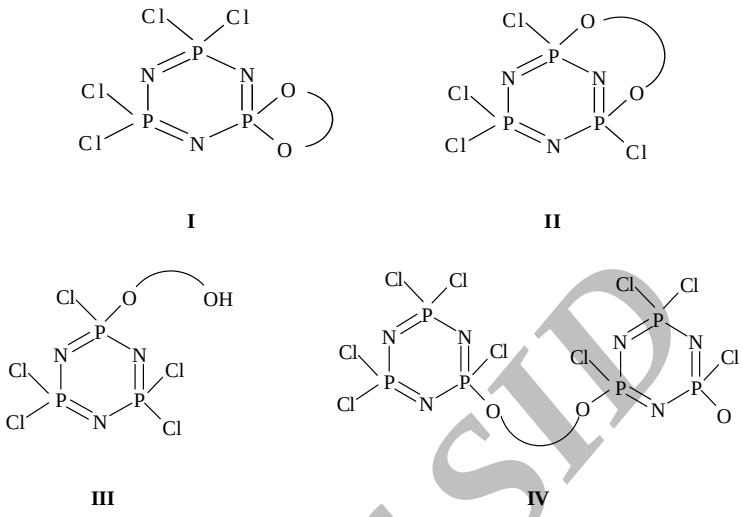
Cyclotriphosphazenes such as $N_3P_3Cl_6$ are among the most well-studied inorganic heterocyclic systems known, and the nucleophilic substitution reactions involving the replacement of labile P-Cl bonds by long bifunctioal phenolic nucleophiles have been extensively investigated [1-3]. The P-Cl bonds can serve as valuable building blocks for developing new microcycles. Additional reactions can be effected on side groups to further increase the functionality [2-4].

The reactive periphery of the cyclotriphosphazenes allows their ready elaboration on a variety of multi-site coordination ligands [5]. One of the main reasons for this is that the phosphazene rings act as a support for the design and supramolecular assembly of ligands.

In general, $N_3P_3Cl_6$ reacts with a non-rigid difunctional reagents such as aliphatic or aromatic diols to yield four different types of products: (i) *spiro* compounds (**I**) (Scheme 1) may form if the difunctional reagent reacts with two geminal chloride atoms, ii) *ansa*, both functional groups of the reagent may replace two chlorine atoms in a *cis* non-geminal arrangement to yield ansa cyclotriphosphazenes (**II**), (iii) dangling, only one of the two functional groups may react with the cyclotriphosphazene to give products with pendent functional units (**III**), (iv) bridging, the dinucleophile may replace two chlorine atoms on different phosphazene rings to link these rings to give oligomers (**IV**), [5-7].

The most promising and rapidly developing aspect in the research on cyclotriphosphazenes is the investigation of the coordination chemistry of ligands bound to the cyclotri-phosphazene core [5,6]. The substituted cyclotriphosphazenes are particularly versatile multimodal ligands which bind to transition metals [7,8]. The wide application of these materials as drug carriers, membranes, polymer solid electrolytes, flame

*Corresponding author. E-mail: tarassoli@scu.ac.ir



*Scheme 1*

retardants, lubricants, catalysts and coating in magnetic tapes is another reason behind the interest in this field [9,10]. The inclusion properties of several *spiro-ansa*-cyclotriphosphazene and phosphazane oligomers are known [11-18].

Earlier**,** we have reported the reaction between the rigid difunctional phenolic ligand 2,3-di-(*O*-hydroxyphenylene) quinoxalin and $N_3P_3Cl_6$ to form the fully *spiro*-substituted product [19]. Recently, we have also reported the aminolysis of $N_3P_3Cl_6$ by bis-[2-ortho-aminophenoxyethyl] ether [20]. This chemistry could be readily adapted for the synthesis of the new derivative of cyclotriphosphazene containing salen side-groups. Accordingly, herein we report the synthesis of the novel tris[bis(salicylidene)ethylenediamine] cyclotriphosphazene, *spiro*-$N_3P_3[(OC_6H_4\text{-}CH{=}N\text{-}CH_2\text{-})_2]_3$ (**1**) and *ansa* (**2**) resulting from the reaction between the ligand bis-salicylidene ethylene diamine ($HOC_6H_4\text{-}CH{=}N\text{-}CH_2\text{-})_2$ (salen) (**3**) and $N_3P_3Cl_6$ (Scheme 2).

## EXPERIMENTAL

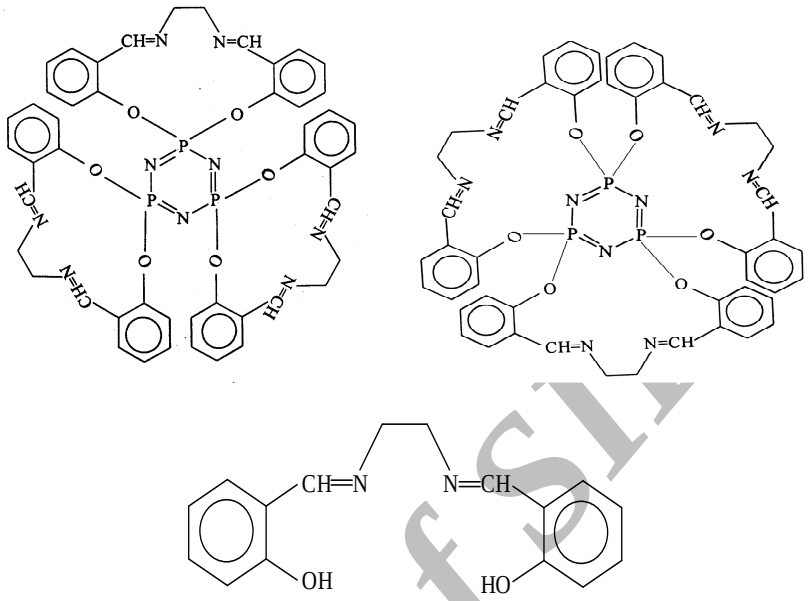
The bis-salicylidene ethylene diamine, salen (**3**) was synthesized according to the method reported in the literature [21]. Tetrahydrofuran and toluene (Merck) were distilled over Na. Hexachlorocyclotriohosphazene (Fluka) was purified from hot petroleum ether and dried in vacuum. Potassium hydroxide and sodium carbonate (Merck) and $Al_2O_3$ (Fluka) were used as received. Other solvents and general reagents used in this work were purified according to the standard procedures.

NMR spectra were recorded on a Bruker Avance 500 MHz at ambient temperature. The $^1H$ and $^{31}P$ NMR chemical shifts were referenced to the residual proton peaks of the deuterated solvents and or tetramethylsilane, TMS, and to the external 85% $H_3PO_4$, respectively. IR spectra were measured on a Bomem FT-IR spectrophotometer which was calibrated with polystyrene film. Elemental analysis was performed by the microanalytical service of National Iranian Oil Company (N.I.O.C) Research Institute of Petroleum Industry, Tehran, Iran.

### Preparation of the Mixture of *Spiro*-$N_3P_3[(OC_6H_4\text{-}CH{=}N\text{-}CH_2\text{-})_2]_3$ (1) and Ansa (2)

A solution of hexachlorocyclotriphosphazenes $N_3P_3Cl_6$ (0.20 g, 0.57 mmol) in THF (15 ml) was added dropwise to a stirring mixture of bis-salicylidene ethylene diamine (salen) (**3**) (0.46 g, 1.71 mmol) and anhydrous sodium carbonate $Na_2CO_3$ (0.36 g, excess) in 25 ml of THF at 25 °C. The reaction mixture was stirred for 8 h at room temperature. Then the mixture was filtered. The solvent was removed and the residue was extracted twice with $CH_2Cl_2$. Evaporation of $CH_2Cl_2$ in vacuo gave the *spiro* (**1**) and *ansa* (**2**) as a yellow solid (yield 82%). The ratio between (**1**) and (**2**) was estimated to be 50:50 from the evaluation of the NMR data.

IR (KBr): 1175-1246 (s, br, P=N), 1632 (sh, s, C=N), 955 (P-O-Ar), 1586, 1488 (C=C aromatic), 756 (CH aromatic),



*Scheme 2*

2875, 2940 ($CH_2$) $cm^{-1}$. $^1H$ NMR (25 °C, DMSO, ppm): 2.64 and 3.08 (s, $CH_2$), 7.26 and 8.35 (s, CH), 6.76-7.38 and 6.93-7.75 (aromatic). $^{31}P\{^1H\}$ NMR (25 °C, DMSO, ppm): -5.9 (s) and -0.8 (s).

### Preparation of Activated $Al_2O_3$

Alumina, $Al_2O_3$ (50 g) (Fluka, pH 7.0 ± 0.5) was added to the solution of KOH (11 g) in 250 ml of distilled water. The mixture was stirred for five minutes and the water was removed. The resulting powder was kept in the oven at 70 °C for 24 h before use [17].

### Synthesis of *Spiro*-$N_3P_3[(OC_6H_4\text{-}CH{=}N\text{-}CH_2\text{-})_2]_3$ (1)

Hexachlorocyclotriphosphazenes $N_3P_3Cl_6$ (0.20 g, 0.57 mmol) and bis-salicylidene ethylene diamine (salen) (0.46 g, 1.71 mmol) in 20 ml of toluene were added to $Al_2O_3$/KOH (1.80 g). The mixture was stirred for 2 h at 25 °C. The solvent was removed and the residue was washed with $CCl_4$ and hexane. Then the product was extracted with 30 ml $CH_3CN$ and filtered. The solvent was evaporated in vacuo. Product (**1**) was obtained as a yellow solid (yield 86%), m.p.: 253 °C. Anal. Calcd. for $C_{48}H_{42}N_9O_6P_3$: C, 34.97; H, 7.65; N, 22.95. Found: C, 34.85; H, 7.61; N, 22.86%.

IR (KBr): 1177, 1247 (s, P=N), 1633 (s, C=N), 928(P-O-Ar), 1488,1587 (C=C aromatic), 760 (CH aromatic), 2881, 2927 ($CH_2$) $cm^{-1}$. $^1H$ NMR (25 °C, DMSO, ppm): 3.08 (s, 12H, $CH_2$), 6.93-7.75 (m, 24H, aromatic), 8.35 (s, 6H, CH). $^{31}P\{^1H\}$NMR (25 °C, DMSO, ppm): -0.7 (s).

## RESULTS AND DISCUSSION

A reaction between $N_3P_3Cl_6$ and difunctional phenolic ligand **(3)** was effected in the ratio of 1:3 in two media: (a) in the two-phase medium in the presence of anhydrous $Na_2CO_3$ used as a base in THF as an aprotic polar solvent and (b) in the two-phase medium containing KOH/$Al_2O_3$ in toluene as an aprotic non-polar solvent. The final arrangements of the products were markedly dependent on the nature of the reaction medium and reagents. It seems that in (a) conditions any configuration of either *spiro* (**1**) or *ansa* (**2**) is obtained along with some amount of the other as the by-product. The reason is the high capacity of $N_3P_3Cl_6$ towards the reaction. On the other hand, in (b) the *spiro* (**1**) arrangement is favored under the aprotic non-polar solvents such as toluene and two-phase medium containing KOH/$Al_2O_3$. In this condition, the alumina holds KOH and subsequently deprotonates the salen

(**3**). Thus, the deprotonated salen immediately attacks the phosphorus atoms of $N_3P_3Cl_6$ and the substitution of P-Cl bonds occurs *via* an associative pathway. After the substitution of one of the chlorines, the remaining P-Cl bonds become more reactive towards affording geminal-substituted products [2]. Similar situation was observed in the aminolysis of hexachlorocyclotriphosphazenes $N_3P_3Cl_6$ [22,23].

The reactions took place at 25 °C, and the manipulations were convenient. The products were obtained with satisfactory yields and they were extensively characterized by IR spectrophotometry as well as $^1H$ and $^{31}P$ NMR techniques. Compound (**1**) was not volatile enough for mass spectrometry due to its high melting point and therefore, reliable mass data were not obtained for this compound.

The PN stretching vibrations in the IR spectrum shifted by almost 28 $cm^{-1}$ relative to $N_3P_3Cl_6$, as a result of the increased electron density on phosphorus upon the replacement of electron-withdrawing chloride substituents with donor oxygen groups on the salen ligands. The appearance of some new bands such as the one at 1633 $cm^{-1}$, which is assigned to C=N in the products, supports the bonding of salen to $P_3N_3$ ring. The IR spectrum also clearly showed the absence of the O-H band at 2650 $cm^{-1}$ and P-Cl bands at 524-601 $cm^{-1}$ region. No bands attributable to O-H or P-Cl groups were detected.

The $^1H$ NMR spectrum of (**1**) clearly shows the presence of the methylene, phenyl and imine protons in the 2.64, 6.76-7.38 and 7.26 ppm, respectively. The appropriate signals in the 50:50 mixture of (**1**) and (**2**) are seen at 2.69 and 3.08, 6.76-7.38 and 6.90-7.70, 7.26 and 8.35 ppm, respectively. The absence of the characteristic OH signal of ligand (**3**) in complexes (**1**) and (**2**) suggests the existence of interaction between salen and $P_3N_3Cl_6$.

The $^{31}P\{^1H\}$ NMR of the 50:50 mixture showed two signals as a singlet peaks at -0.8 and -5.9 ppm with equal intensity which was attributed to the chemically equivalent phosphoruses in *spiro* (**1**) and also in *ansa* (**2**) configuration, respectively. It is also of interest to note that the $^{31}P\{^1H\}$ NMR spectrum of the *spiro* (**1**) shows only one sharp singlet at -0.7 ppm, indicating the formation of a single species, with the phosphorus chemical shift consistent with the *spiro* (**1**) structure [22,24]. Due to the high capacity of hexachlorocyclotriphosphazenes to bind to salen in THF, it was not possible to obtain *spiro* (**1**) or *ansa* (**2**) as unique pure products. However, the regiospecificity of the reaction was considerably improved by employing activated alumina in toluene to obtain exclusively *spiro* (**1**) in an excellent yield.

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## REFERENCES

[1] H.R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, 1972.

[2] K. Brandt, I. Porwolik-Czomperlik, M. Siwy, T. Kupka, R.A. Shaw, D.B. Davies, R. Bartsch, J. Incl. Phenom. Macro. Chem. 35 (1999) 281.

[3] E.W. Ainscough, A.M. Brodie, R.J. Davidson, C.A. Otter, Inorg. Chem. Commu. 11 (2008) 171.

[4] C. Nataro, C.N. Myer, W.M. Cleaver, C.W. Allen, J. Organomet. Chem. 637-639 (2001) 284.

[5] V. Chandrasekhar, B.M. Pandian, R. Azhakar, Polyhedron 27 (2008) 255.

[6] E.W. Ainscough, A.M. Brodie, R.J. Davidson, C.A. Otter, Inorg. Chem. Commun. 10 (2007) 1005.

[7] E.W. Ainscough, A.M. Brodie, C.V. Depree, C.A. Otter, Polyhedron 25 (2006) 2341.

[8] N. Thirupathi, S.S. Krishnamurthy, M. Nethaji, Polyhedron 18 (1999) 437.

[9] K.L. Rule, I.I. Selvaraji, R.L. Kirchmeier, J. Fluorine Chem. 112 (2001) 307.

[10] G.A. Carriedo, F.J. Garcia Alonso, P.A. Gonzalez, P. Gomez-Elipe, Polyhedron 18 (1999) 2853.

[11] F. Sournies, J.F. Labarre, Inorg. Chim. Acta 90 (1984) L61.

[12] M. Pietraszkiewicz, A. Klonkowski, K. Staniszewski, J. Karpiuk, S. Bianketti, O. Pietraszkiewicz, J. Incl. Phenom. Macro. Chem. 49 (2004) 61.

[13] K. Kubono, H. Kurata, S. Isoda, T. Kobayashi, J. Matter. Chem. 3 (1993) 615.

[14] V. Chandrasekhar, V. Krishnan, A. Athimoolam, G.T.S. Andavan, Can. J. Chem. 80 (2002) 1415.

[15] A. Comotti, M.C. Gallazzi, R. Simonutti, P. Sozzani, Chem. Matter. 10 (1998) 3589.

[16] A. Tarassoli, G. Emami, Z. khodamoradpur, Phosphorus, Sulfur and Silicon 182 (2007) 2497.
[17] A. Tarassoli, M.L. Thompson, R.C. Haltiwanger, T.G. Hill, A.D. Norman, Inorg. Chem. 27 (1988) 3382.
[18] A. Tarassoli, H.J. Chen, M.L. Thompson, V.S. Allured, R.C. Haltiwanger, D. Norman, Inorg. Chem. 25 (1986) 4152.
[19] A. Tarassoli, M.R. Shushizadeh, Phosphorus Sulfur and Silicon 178 (2003) 803.
[20] A. Tarassoli, T. Sedaghat, H.R. Goudarzi, Cent. Eur. J. Chem. 7 (2009) 130.
[21] Q.P. Fieffer, T. Hess, P.H. Fitzer, W. Scohll, H. Thielert, J. Prak. Chem. 149 (1937) 217.
[22] F. Sournies, J.F. Labarre, Inorg. Chim. Acta 268 (1998) 307.
[23] V. Chandrasekhar, P. Thilagar, B.M. Pandian, Coord. Chem. Rev. 251 (2007) 1045.
[24] M.C. Labarre, J.F. Labarre, J. Mole. Struct. 300 (1993) 593.