**DE GRUYTER** Z. Naturforsch. 2018; aop

Mohammad Hakimi*, Homeyra Rezaei, Keyvan Moeini, Heidar Raissi, Vaclav Eigner and Michal Dušek

# Microwave-assisted solvent-free synthesis and spectral and structural characterization of cyclotriphosphazene hexakis(*o*-tolylamide)

https://doi.org/10.1515/znb-2018-0136
Received June 29, 2018; accepted October 2, 2018

**Abstract:** A new cyclotriphosphazene, 2,2,4,4,6,6-hexakis (*o*-tolylamono)-1,3,5,2$\lambda^5$,4$\lambda^5$,6$\lambda^5$-triazatriphosphinine (MPAP), was prepared using microwave irradiation and identified by elemental analysis, FT-IR, Raman, $^{31}$P NMR spectroscopy, and single-crystal X-ray diffraction. In the crystal, in addition to hydrogen bonds, the network is further stabilized by inter- and intramolecular π–π stacking interactions between aromatic rings.

**Keywords:** crystal structure; cyclotriphosphazene; microwave; $^{31}$P NMR.

## 1 Introduction

Phosphazenes are compounds containing a phosphorus–nitrogen double bond in their skeleton. They are well known as iminophosphoranes and phosphine imides. Phosphazenes fall into three categories: cyclo-, poly-, and monophosphazenes. Cyclo- and polyphosphazenes are very well known and have been intensively studied because they are more stable than monophosphazenes [1]. The properties of phosphazenes can be changed over a wide range by attaching different substituents to the main backbone [2]. The synthesis of phosphazene compounds has become important because these compounds have many potential applications, including as biomaterials [3], drug delivery systems [4], fuel cell membranes [5, 6], gas membranes [7], ionic conductors [8], flame retardants [9], and optical materials [7, 10], and in ion separation [11].

In order to extend the chemistry of the cyclotriphosphazene, in this work we describe the synthesis of a new derivative, 2,2,4,4,6,6-hexakis(*o*-tolylamino)-1,3,5,2$\lambda^5$,4$\lambda^5$,6$\lambda^5$-triazatriphosphinine (MPAP, Scheme 1), along with its characterization including elemental analysis, FT-IR, Raman, and $^{31}$P NMR spectroscopy.

## 2 Results and discussion

The reaction between hexachlorocyclotriphosphazene and an excess of *o*-toluidine under microwave irradiation [12–15] and solvent-free conditions gave MPAP in good yields. This compound is air-stable and soluble in ethanol and DMSO.

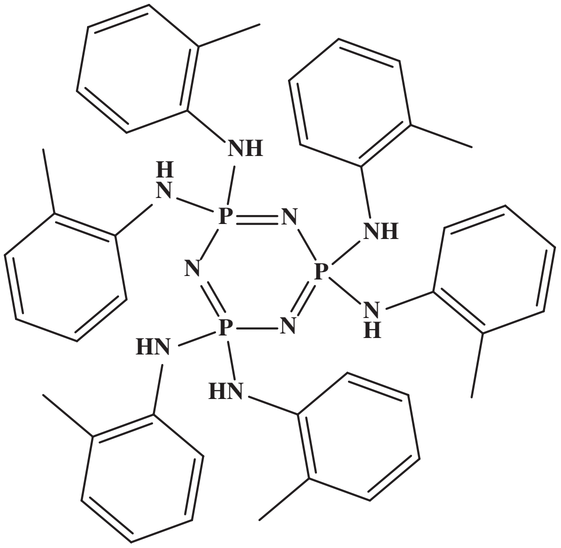
### 2.1 Spectroscopic studies

In the IR spectrum of the compound, frequencies below and above 3000 cm$^{-1}$ and also at 3300 cm$^{-1}$ can be assigned to the stretching vibrations of the C–H and N–H bonds, confirming the presence of the aliphatic, aromatic, and amine moieties, respectively, in MPAP. These vibrations confirm the successful substitution of *o*-toluidine on hexachlorocyclotriphosphazene. The FT-IR and Raman spectra of MPAP show two intense absorption signals at 1157 and 937 cm$^{-1}$, which are attributed to the asymmetric and symmetric stretching vibrations of the P=N bonds in the phosphazene ring, respectively [16, 17]. In the low-frequency region, the phosphazene ring exhibits four other types of vibrations, namely bending, wagging, twisting, and rocking, in the order $(\delta_{\text{bend}}\ \text{PN})^{\text{ring}} > (\delta_{\text{wag}}\ \text{PN})^{\text{ring}} > (\delta_{\text{rock}}\ \text{PN})^{\text{ring}} > (\delta_{\text{bend}}\ \text{NPN}) > (\delta_{\text{twist}}\ \text{NPN})$ [16].

The $^{31}$P NMR spectrum of MPAP shows an intense single peak at $\delta = 5.12$ ppm. This shows that the three phosphorus atoms in the compound have the same chemical environment, which can happen only with the symmetric substitution of all the chlorine atoms. Comparing

---

***Corresponding author: Mohammad Hakimi,** Chemistry Department, Payame Noor University, Tehran 19395-4697, I. R. Iran, Fax: +98 44 32768825, E-mail: mohakimi@yahoo.com
**Homeyra Rezaei and Keyvan Moeini:** Chemistry Department, Payame Noor University, Tehran 19395-4697, I. R. Iran
**Heidar Raissi:** Chemistry Department, Birjand University, Shokat Abad-Pardis-e-Daneshgag, Birjand, South Khorasan 13179, I. R. Iran
**Vaclav Eigner and Michal Dušek:** Institute of Physic of the Czech Academy of Sciences, Na Slovance 2, Prague 182 21, Czech Republic



**Scheme 1:** Structure of the MPAP molecule.

**Table 1:** Selected bond lengths (Å) and angles (deg) for MPAP with estimated standard deviations in parentheses.

| Bond lengths | | Angles | |
|---|---|---|---|
| N1–P1 | 1.5897(9) | N1–P3–N3 | 116.64(5) |
| N1e–P3 | 1.661(1) | N1b–P1–N1a | 103.11(5) |
| N2–P2 | 1.5937(8) | N1d–P2–N1c | 100.02(5) |
| N3–P3 | 1.6054(9) | N1f–P3–N1e | 102.11(5) |
| N2–P1 | 1.6118(9) | N2–P1–N1 | 116.77(4) |
| N1a–P1 | 1.654(1) | N3–P2–N2 | 117.59(5) |
| N1b–P1 | 1.664(1) | P1–N1–P3 | 123.67(5) |
| N3–P2 | 1.5918(9) | P2–N2–P1 | 121.75(5) |
| N1c–P2 | 1.676(1) | P3–N3–P2 | 121.51(6) |
| N1d–P2 | 1.6629(9) | | |
| N1–P3 | 1.5833(8) | | |
| N1f–P3 | 1.666(1) | | |

The suffixes a, b, c, d, e, f denote crystallographically distinct *o*-toluidine groups.

the $^{31}P$ NMR spectra of hexachlorocyclotriphosphazene ($\delta = 0.60$ ppm) and MPAP ($\delta = 5.12$ ppm), the latter shows a shift of $\Delta\delta = 4.52$ ppm to lower magnetic field.

## 2.2 Crystal structure of MPAP

The single-crystal X-ray diffraction analysis of the MPAP (Fig. 1) confirmed the full substitution of the chlorine atoms on the cyclotriphosphazene ring by *o*-toluidine groups. The core of the molecule is a six-membered ring N1–P1–N2–P2–N3–P3 with the bond lengths averaging 1.596 Å, which is smaller than the average length of the newly created P–N single bonds (1.664 Å). The average of the P–N–P bond angles of the ring in MPAP is 122.3°, i.e. smaller than the average N–P–N bond angles of the same ring (117.0°). On the other hand, the average N–P–N bond angles between the *o*-toluidine groups are smaller (101.8°) than the endocyclic angles. The average bond angles around the phosphorus atoms reveal distorted tetrahedral geometries (Table 1). The rms value from the mean plane through the cyclotriphosphazene ring shows that the ring slightly deviates from planarity (0.092 Å for the N3 atom).

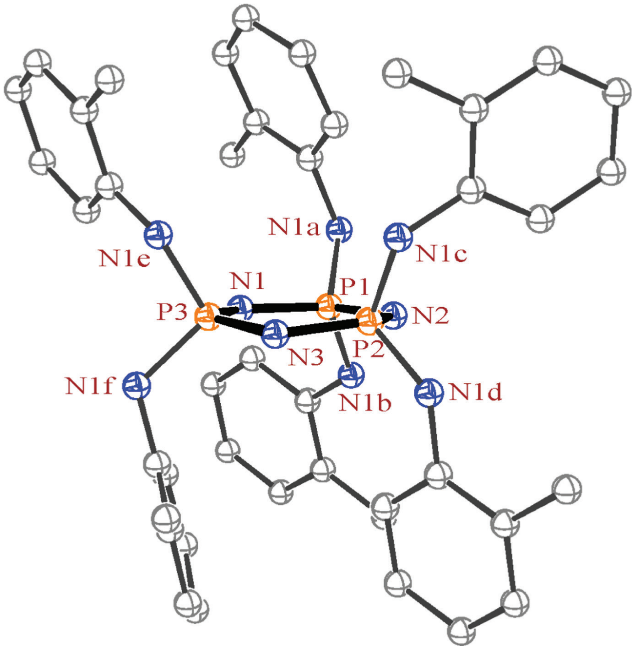


**Fig. 1:** ORTEP-III diagram of the molecular structure of MPAP. The ellipsoids are drawn at the 35% probability level.

In the crystal network of MPAP, there are weak intermolecular C–H···N and N–H···N hydrogen bonds between adjacent molecules (Fig. 2) in which the carbon atoms act as proton donors while the nitrogen atoms are both proton donors and acceptors. Among the intermolecular contacts, the aromatic rings of the *o*-toluidine moieties appear to play a significant role by participating in the formation of the C–H···π (Table 2) and π–π stacking (Table 3) interactions [18, 19]. Based on the centroid–centroid distances between the aromatic rings, these intermolecular π–π stacking interactions (Fig. 2) are stronger than the intramolecular ones.

## 3 Conclusion

A new cyclotriphosphazene, MPAP, was prepared and its spectral (IR, Raman, $^{31}P$ NMR) and structural (single-crystal X-ray diffraction) properties were investigated.

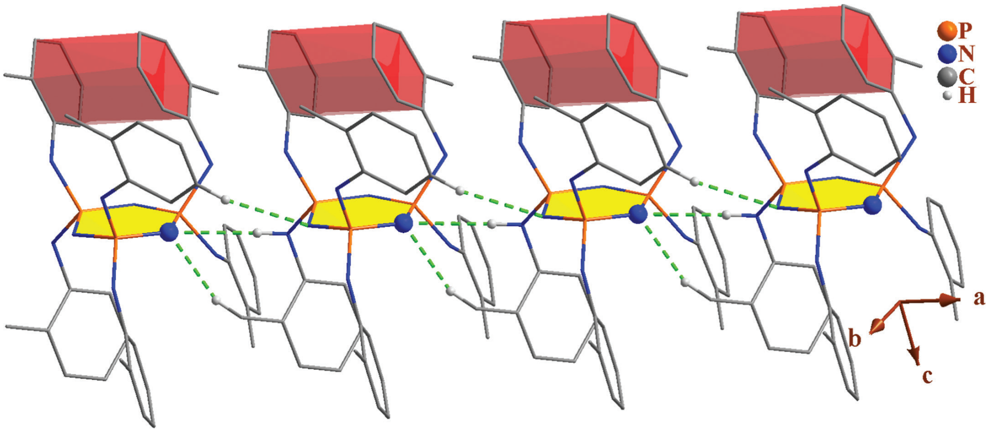


**Fig. 2:** Packing of MPAP molecules in the crystal, showing the hydrogen bonds and π–π stacking interactions. Only the hydrogen atoms involved in hydrogen bonding are shown.

**Table 2:** Hydrogen bond dimensions (Å and deg) in MPAP.

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | <(DHA) | Symmetry code of A |
|---|---|---|---|---|---|
| C5c–H1c5c···N3 | 0.960 | 2.7282 | 3.479(1) | 135.54 | 1 + *x*, *y*, *z* |
| C7f–H2c7f···N2 | 0.960 | 2.7387 | 3.657(1) | 160.38 | −1 + *x*, *y*, *z* |
| N1f–H1n1f···N2 | 0.86 | 2.612 | 3.424(1) | 158 | −1 + *x*, *y*, *z* |
| C7f–H3c7f···π | 0.960 | 3.098 | 3.592 | 113.63 | |
| C7b–H1c7b···π | 0.960 | 2.595 | 3.536 | 166.57 | |
| C5b–H1c5b···π | 0.960 | 2.868 | 3.694 | 144.84 | |

**Table 3:** π–π stacking interactions (Å and deg) in MPAP.

| Centroid–centroid distance | Angle between the planes | Type of interaction |
|---|---|---|
| 3.899 | 7.22 | Intramolecular |
| 3.851 | 7.22 | Intermolecular |

In the crystal structure of the MPAP, the bond angles of the phosphorus atoms revealed a distorted tetrahedral geometry around these atoms. In addition to the C–H···N and N–H···N hydrogen bonds in the crystal network, the structure features both inter- and intramolecular interactions between aromatic rings in a form of π–π stacking and C–H···π interactions.

# 4 Experimental

## 4.1 Materials and measurements

All chemicals and solvents were used as received without further purification. Carbon, hydrogen, and nitrogen contents were determined using a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Infrared spectra (as KBr pellets) were recorded from 400 to 4000 $\mathrm{cm^{-1}}$ using an FT-IR 8400 Shimadzu spectrometer. Melting point was determined using a Barnsted Electrothermal 9200 electrically heated apparatus. $^{31}$P NMR spectrum was recorded on a Bruker Aspect 3000 instrument operating at 300 MHz, and chemical shifts are given in parts per million with reference to an internal standard of phosphoric acid. The microwave-assisted synthesis of the title compound was carried out using a Microwave Laboratory Systems MicroSYNTH (Milestone s.r.l.)

## 4.2 Preparation of MPAP

Dry and pure hexachlorocyclotriphosphazene (0.35 g, 1 mmol) was added to 3.00 g (28 mmol) of *o*-toluidine and irradiated in the synthetic microwave oven under reflux and under solvent-free conditions for 2 h with a power 200 W. Then the reaction mixture was allowed to cool down to room temperature. The product was extracted with chloroform and water three times. The reaction product was in the phase of chloroform and the amine salt by-product in the water phase. After evaporation of chloroform at ambient temperature, the desired product was obtained. Finally, the product was recrystallized from methanol to produce colorless crystals. Yield 0.46 g, 60%; m. p. 150°C. Anal. calcd. for $C_{42}H_{48}N_9P_3$ (771.83): C 65.36, H 6.27, N 16.33; found C 65.84, H 6.36, N 16.43%. IR (KBr): $\nu = 3310$ m (N–H), 3007 w $(\text{C–H})^{\text{ar}}$, $\nu_{as} = 2950$ w $(\text{CH}_3)$, $\nu = 1497$ m $(\text{C=C})^{\text{ar}}$, $\delta_{as} = 1465$ w $(\text{CH}_3)$, $\delta_s = 1369$ m $(\text{CH}_3)$, $\nu_{as} = 1157$ s $(\text{P=N})^{\text{ring}}$, $\nu = 1107$ m (C–N), $\nu_s = 937$ m $(\text{P=N})^{\text{ring}}$, $\delta_{bend} = 714$ m $(\text{P=N})^{\text{ring}}$, 617 w $\delta_{wag} = (\text{PN})^{\text{ring}}$, $\delta_{rock} = 536$ w

$(P=N)^{ring}$, $\delta_{bend} = 465$ w (N–P–N) cm$^{-1}$. Raman: $\delta_{as} = 1415$ m ($CH_2$), $\nu_{as} = 1172$ m $(PN)^{ring}$, $\nu = 1049$ s (C–N), $\nu_s = 894$ m $(P=N)^{ring}$, $\delta_{bend} = 712$ m $(P=N)^{ring}$, $\delta_{rock} = 588$ s $(P=N)^{ring}$, $\delta_{bend} = 432$ m (N–P–N), $\delta_{twist} = 154$ s (N–P–N) cm$^{-1}$. $^{31}P$ NMR (250 MHz, $CDCl_3$): $\delta = 5.12$ ppm.

### 4.3 Crystal structure determination

A suitable crystal of MPAP was chosen, and its X-ray diffraction analysis was performed at $T = 95$ K using a SuperNova diffractometer equipped with a micro-focus sealed tube, mirror-collimated Cu K$\alpha$ radiation ($\lambda = 1.54184$ Å), and a CCD detector (Atlas S2). The data was processed with CrysAlis [20]. The structure was solved with the charge flipping algorithm Superflip [21] and refined by full-matrix least-squares on $F^2$ using the program Jana2006 [22]. Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms on carbon were kept at geometrically expected positions and refined as riding atoms with $U_{iso} = 1.2\ U_{eq}$ of the corresponding parent atom. Positions of hydrogen atoms on nitrogen were refined using the N–H bond length restraint 0.86 Å with s.u. of the constraint = 0.001 and $U_{iso} = 1.2\ U_{eq}$ of the corresponding parent atom. Diagrams of the molecular structure and unit cell were created using the programs Ortep [23, 24] and Diamond [25]. Crystal data and details of the data collection and refinement are given in Table 4. Selected bond lengths and angles of the compound are listed in Table 1 and the hydrogen bond geometries in Table 2.

CCDC 1842613 (MPAP) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table 4:** Crystal data and structure refinement for MPAP.

| | |
|---|---|
| Empirical formula | $C_{42}H_{48}N_9P_3$ |
| Formula weight, g mol$^{-1}$ | 771.8 |
| Crystal size, mm$^3$ | 0.37 × 0.09 × 0.06 |
| Temperature, K | 95 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | |
| *a*, Å | 7.6535(1) |
| *b*, Å | 20.3655(2) |
| *c*, Å | 24.7152(3) |
| $\beta$, deg | 94.1974(10) |
| Volume, Å$^3$ | 3841.96(8) |
| *Z* | 4 |
| Calculated density, g cm$^{-3}$ | 1.33 |
| Absorption coefficient, mm$^{-1}$ | 1.8 |
| *F*(000), *e* | 1632 |
| $\theta$ range for data collection, deg | 3.6–76.3 |
| *hkl* ranges | $-9 \le h \le 9$, $-25 \le k \le 25$, $-30 \le l \le 31$ |
| Reflections collected/independent/$R_{int}$ | 58421/8022/0.032 |
| Data/restraints/parameters | 8022/6/506 |
| $R1/wR2$ [$I > 3\sigma(I)$] | 0.0290/0.0923 |
| $R1/wR2$ (all data) | 0.0312/0.0940 |
| Goodness of fit on $F^2$ | 1.85[a] |
| Largest diff. peak/hole, *e* Å$^{-3}$ | 0.31/−0.35 |

[a] Jana2006 does not refine the weighting scheme. Therefore, the goodness of fit is usually fairly above 1, especially for well-exposed data, bearing information about the bonding electrons.

## 5 Supporting information

$^{31}P$ NMR, FT-IR, and Raman spectra of MPAP and the $^{31}P$ NMR spectrum of hexachlorocyclotriphosphazene are given as supplementary material available online (DOI: 10.1515/znb-2018-0136).

## References

[1] E. Çil, M. Arslan, F. Aslan, A. I. Öztürk, *Phosphorus Sulfur Silicon Relat. Elem.* **2003**, *178*, 1037.

[2] H. R. Allcock, *Chemistry and Application of Phosphazenes*, Wiley Interscience, New York, **2003**.

[3] J. H. Goedemoed, K. De Groot, A. M. E. Claessen, R. J. Scheper, *J. Control. Release* **1991**, *17*, 235.

[4] Y. S. Sohn, Y. J. Jun in *Polyphosphazenes for Biomedical Applications* (Ed.: A. K. Andrianov), John Wiley, Hoboken, New Jersey, **2009**, p. 249.

[5] H. Tang, P. N. Pintauro, *J. Appl. Polym. Sci.* **2001**, *79*, 49.

[6] G. Dotelli, M. C. Gallazzi, C. M. Mari, F. Greppi, E. Montoneri, A. Manuelli, *J. Mater. Sci.* **2004**, *39*, 6937.

[7] M. Gleria, R. D. Jaeger, *Phosphazenes A Worldwide Insight*, Nova Science Publishers, New York, **2004**.

[8] K. Inoue, T. Yamauchi, T. Itoh, E. Ihara, *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 367.

[9] C. S. Reed, J. P. Taylor, K. S. Guigley, M. M. Coleman, H. R. Allcock, *Polym. Eng. Sci.* **2000**, *40*, 465.

[10] M. A. Olshavsky, H. R. Allcock, *Macromolecules* **1995**, *28*, 6188.

[11] C. A. Allen, D. G. Cummings, A. E. Grey, R. E. Mcatee, R. R. Mccaffrey, *J. Membr. Sci.* **1987**, *33*, 181.

[12] M. Hakimi, Z. Mardani, K. Moeini, F. Mohr, E. Schuh, H. Vahedi, *Z. Naturforsch.* **2012**, *67b*, 452.

[13] M. Hakimi, Z. Mardani, K. Moeini, E. Schuh, F. Mohr, *Z. Naturforsch.* **2013**, *68b*, 267.

[14] M. Hakimi, Z. Mardani, K. Moeini, E. Schuh, F. Mohr, *Z. Naturforsch.* **2013**, *68b*, 272.

[15] M. Hakimi, Z. Mardani, K. Moeini, M. Minoura, H. Raissi, *Z. Naturforsch.* **2011**, *66b*, 1122.

[16] M. Gobel, K. Karaghiosoff, T. M. Klapotke, *Angew. Chem. Int. Ed.* **2006**, *45*, 6037.
[17] A. Okumus, S. Bilge, Z. Kilic, A. Ozturk, T. Hokelek, F. Yilmaz, *Spectrochim. Acta* **2010**, *A76*, 401.
[18] F. Marandi, K. Moeini, B. Mostafazadeh, H. Krautscheid, *Polyhedron* **2017**, *133*, 146.
[19] M. Hakimi, Z. Mardani, K. Moeini, F. Mohr, *Polyhedron* **2015**, *102*, 569.
[20] CrysAlisPro Software system (version 1.171.38.43), Rigaku Oxford Diffraction, Rigaku Corporation, Oxford (UK) **2018**.
[21] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
[22] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr. – Cryst. Mater.* **2014**, *229*, 345.
[23] M. N. Burnett, C. K. Johnson, ORTEP-III, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, TN (USA) **1996**.
[24] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[25] G. Bergerhoff, M. Berndt, K. Brandenburg, *J. Res. Natl. Stand. Technol.* **1996**, *101*, 221.

**Supplementary Material:** The online version of this article offers supplementary material (https://doi.org/10.1515/znb-2018-0136).

# Graphical synopsis

Mohammad Hakimi, Homeyra Rezaei,
Keyvan Moeini, Heidar Raissi,
Vaclav Eigner and Michal Dušek

**Microwave-assisted solvent-free synthesis and spectral and structural characterization of cyclotriphosphazene hexakis(*o*-tolylamide)**

https://doi.org/10.1515/znb-2018-0136
Z. Naturforsch. 2018; x(x)b: xxx–xxx