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DESIGNATION OF ABSOLUTE CONFIGURATION OF MULTI-HETEREOCYCLIC 9,13-DICHLORO-22,22-DIPYRROLIDINE-1-YL-1H,2H,13H,19H-9,13-(EPIAZENOPHOSPHAZENO)-9λ5,11λ5,13λ5-[1,3,5,2,4] BENZOXADIAZADİPHOSPHONINO[4 ,5 :2,3][1,3,2]DIAZAPHOSPHOLO[2,1-D][1,3,5,2,4]BENZOXADIAZADIPHOSPHONINE BY X-RAY CRYSTALLOGRAPHIC DATA

GAMZE ELMAS, AYTUĞ OKUMUŞ, SATİYE SEVİM İSAOĞLU, TUNCER HÖKELEK AND ZEYNEL KILIÇ

Abstract. The title compound, 9,13-dichloro-22,22-dipyrrolidine-1-yl-1*H*,2*H*,13*H*,19*H*-9,13-(epiazenophosphazeno)-9λ^5,11λ^5,13λ^5-[1,3,5,2,4]benzoxadiazadiphosphonino [4',5':2,3][1,3,2]diazaphospholo[2,1-*d*][1,3,5,2,4]benzoxadiazadiphosphonine; 2($C_{24}H_{32}Cl_2N_8O_2P_4$). 0.5 C_6H_{12}, a cyclotetraphosphazene derivative, has a *geminal*-dipyrrolidino-2-*trans*-6-dichloro-*ansa-spiro-ansa* (***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa**) structure in which the tricyclic parts are consisted of three eight-membered rings, containing a tetrameric N_4P_4 and two ansa rings. However, all these rings are not planar. The asymmetric unit contains two crystallographically independent molecules and one half of the cyclohexane solvent molecule. In both molecules, it is expected that two P (P1 and P3/P1′ and P3′) atoms are stereogenic centres. Both ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** molecules have *trans* structures according to the Cl atoms, and they are in the racemic forms. Besides, it is found that the absolute configurations of P1, P3 and P1′, P3′ phosphorus centers are RR and SS, respectively. The title compound has *P-1* space group, a Sohncke chiral space group, with the cell parameters of a = 9.6682(2), b = 13.8587(3), c = 24.0250(4) Å, α = 105.249(2)°, β = 96.298(3)° and γ = 98.367(3)°.

1. Introduction

Octachlorocyclotetraphosphazene ($N_4P_4Cl_8$, tetramer) is a standard starting material for the preparation of the new cyclotetraphosphazene derivatives [1,2]. It has eight reactive P-Cl bonds, and these Cl atoms may exchange with a number of substituents, such as monodentate (amines and alkoxides), bidentate (diamines, dialkoxides and aminoalkoxides) and multidentate (polyamines, polyalkoxides and polyaminoalkoxides) ligands [3-5]. In addition, it is difficult to study the substitution reactions of $N_4P_4Cl_8$ with these ligands because of the formation of a large number of products (*cis*/*trans*-, spiro-, ansa-, bino- and optical isomers)

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and also because of the difficulties faced in the separations of these isomers from the reaction mixtures. However, in the literature, the number of the reported Cl substitution reactions with multidentate ligands containing N_2O_2 and N_2N_2 donor atoms are much less than the others [5-7].

The chiralities of the cyclophosphazenes have been researched recently as an interesting topic [8,9]. However, there are fairly a few studies researching the chiralities of the cyclotetraphosphazenes using different methods, eg. X-ray crystallography, ^{31}P NMR spectroscopy in the presence of (R)-(+)-2,2,2-trifluoro-1-(9'-anthryl)-ethanol (CSA) and HPLC in the literature [9-11].

On the other hand, in recent years, organocyclophosphazene derivatives have attracted so much attention by means of their different and special applications in some areas; such as liquid crystals [12], thermal stabilities [13], fluorescence chemosensors [14], membranes [15], the oxidative DNA cleavages [16], the antituberculosis [17], anti-cancer [18], antibacterial [19] and antifungal [20] reagents.

Herein, the title compound was prepared from the reaction of pyrrolidine with tetrachloro-2,4,6-ansa-spiro-ansa (**tetrachloro-asa)** product [21] obtained from the reaction of $N_4P_4Cl_8$ and N_2O_2 donor-type unsymmetrical tetradentate ligand with respect to the literature method. The goal of the present paper is to research the crystallographic and stereogenic properties of **dichloro-dipyrrolidino-asa** cyclotetraphosphazene.

2. Materials And Methods

2.1. X-ray crystal structure determinations

The colourless crystals of the **dichloro-dipyrrolidino-asa** compound were recrystallized from cyclohexane-THF (6:1) at room temperature. The crystallographic data are presented in Table 1, and the selected bond lengths and angles with the torsion angles are listed in Table 2. The crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K_α radiation (λ=0.71073 Å) at T=100(2) K. Absorption correction by multi-scan [22] was applied. Structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data [23]. All non-H atoms were refined anisotropically. The remaining H atom positions were calculated geometrically at distances of 0.93 Å (CH) and 0.97 Å (CH_2) from the parent C atoms; a riding model was used during the refinement process and the U_{iso}(H) values were constrained to be $1.2U_{eq}$(carrier atom).

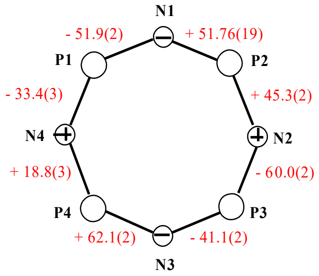
2.2. Materials used for syntheses

According to the published paper, the beginning N_2O_2 tetradentate ligand, {2,2'-[1,2-ethanediylbis(iminomethanediyl)]diphenol}, the starting cyclotetraphosphazene {**tetrachloro-asa**} and the title product {***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa**} were synthesized again [21].

TABLE 1. Crystallographic details.

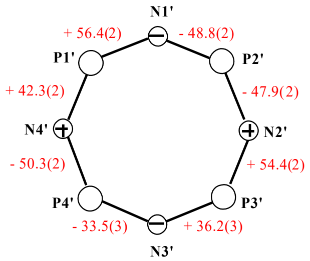
Empirical Formula	$2(C_{24}H_{32}Cl_2N_8O_2P_4).\ 0.5\ C_6H_{12}$
Fw	1360.79
Crystal System	triclinic
Space Group	*P -1*
a (Å)	9.6682(2)
b (Å)	13.8587(3)
c (Å)	24.0250(4)
α (°)	105.249(2)
β (°)	96.298(3)
γ (°)	98.367(3)
V (Å^3)	3035.54(10)
Z	2
T	100(2) K
Crystal color	colorless
Crystal size	0.15x0.35x0.43 mm
μ (mm^{-1})	0.466 (Mo K_α)
ρ (calcd) (g cm^{-3})	1.489
Number of Reflections Total	14920
Number of Reflections Unique	10169
R_{int}	0.0813
$(\Delta/\sigma)_{max}$	<0.001
$(\Delta\rho)_{max}$	1.111 e Å^{-3}
$(\Delta\rho)_{min}$	−1.282 e Å^{-3}
$2\theta_{max}$ (°)	56.74
T_{min} / T_{max}	0.825 / 0.933
Number of Parameters	748
R [$F^2 > 2\sigma(F^2)$]	0.0467
wR	0.1041

TABLE 2. The selected bond lengths (Å) and angles (°) with the torsion angles (°).

Molecule I					
P1– N1	1.564(2)	N1– P1– N4	125.73(11)	N4– P1– N1– P2	-51.9(2)
P1– N4	1.547(2)	N1– P2– N2	113.54(11)	N3– P3– N2– P2	-60.0(2)
P2– N1	1.598(2)	N2– P3– N3	124.00(11)	N1– P2– N2– P3	45.3(2)
P2– N2	1.602(2)	N3– P4– N4	116.20(11)	N2– P2– N1– P1	51.76(19)
P3– N3	1.561(2)	P1– N1– P2	128.21(15)	N2– P3– N3– P4	-41.1(2)
P3– N2	1.568(2)	P3– N2– P2	126.58(15)	N4– P4– N3– P3	62.1(2)
P4– N3	1.606(2)	P1– N4– P4	133.44(15)	N1– P1– N4– P4	-33.4(3)
P4– N4	1.599(2)	P3– N3– P4	125.30(14)	N3– P4– N4– P1	18.8(3)
P1– O1	1.6046(17)	N4– P1– O1	103.67(11)		
P2– N5	1.650(2)	N6– P2– N2	114.37(11)		
P2– N6	1.639(2)	N6– P2– N1	108.32(12)		
P4– N7	1.627(2)	N5– P2– N1	115.02(11)		
P4– N8	1.646(2)	N5– P2– N6	95.22(11)		
P1– Cl1	2.0465(10)	N3– P3– O2	103.92(11)		
P3– Cl2	2.0419(9)	N7– P4– N8	103.49(11)		

Molecule II

P1′– N1′	1.565(2)	N1′– P1′– N4′	124.34(11)	N4′– P1′– N1′– P2′	56.4(2)
P1′– N4′	1.552(2)	N1′– P2′– N2′	113.79(11)	N3′– P3′– N2′– P2′	54.4(2)
P2′– N1′	1.598(2)	N2′– P3′– N3′	125.38(11)	N1′– P2′– N2′– P3′	-47.9(2)
P2′– N2′	1.605(2)	N3′– P4′– N4′	116.43(11)	N2′– P2′– N1′– P1′	-48.8(2)
P3′– N3′	1.548(2)	P1′– N1′– P2′	127.39(15)	N2′– P3′– N3′– P4′	36.2(3)
P3′– N2′	1.562(2)	P3′– N2′– P2′	127.72(15)	N4′– P4′– N3′– P3′	-33.5(3)
P4′– N3′	1.602(2)	P1′– N4′– P4′	128.58(14)	N1′– P1′– N4′– P4′	42.3(2)
P4′– N4′	1.599(2)	P3′– N3′– P4′	132.24(15)	N3′– P4′– N4′– P1′	-50.3(2)
P1′– O1′	1.5962(18)	N4′– P1′– O1′	103.58(11)		
P2′– N5′	1.647(2)	N6′– P2′– N2′	114.45(11)		
P2′– N6′	1.648(2)	N6′– P2′– N1′	108.11(12)		
P4′– N7′	1.637(2)	N5′– P2′– N1′	114.98(11)		
P4′– N8′	1.629(2)	N5′– P2′– N6′	95.51(11)		
P1′– Cl1′	2.0483(9)	N3′– P3′– O2′	103.45(11)		
P3′– Cl2′	2.0482(10)	N7′– P4′– N8′	103.67(11)		



3. Result And Discussion

The title compound (Fig. 1) is a cyclotetraphosphazene derivative with a bulky N_2O_2 tetradentate ligand attached through the 2,4,6-ansa-spiro-ansa junction, where two pyrrolidine groups are bonded to the same phosphorus atom in a *geminal* position and two Cl atoms bonded to the different phosphorus atoms in a *non-geminal-trans* manner. The asymmetric unit contains two independent molecules (molecule I and molecule II) and one-half of the cyclohexane solvent molecule. The molecules, I and II, have two equivalent stereogenic P centers (P1, P3 and P1′, P3′), and it is expected that they are in the racemic mixture (RR/SS) because of the *trans*- position of two Cl atoms (Fig. 1). It is undoubtedly found that the absolute configurations of both molecules are RR (for P1 and P3 atoms of molecule I) and SS (for P1′ and P3′ atoms of molecule II). As a result, it is determined that both enantiomers are together in the solid-state. Furthermore, the space group of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** is *P-1.* It is among the Sohncke space groups, and the chiral properties of them are investigated in the literature [24].

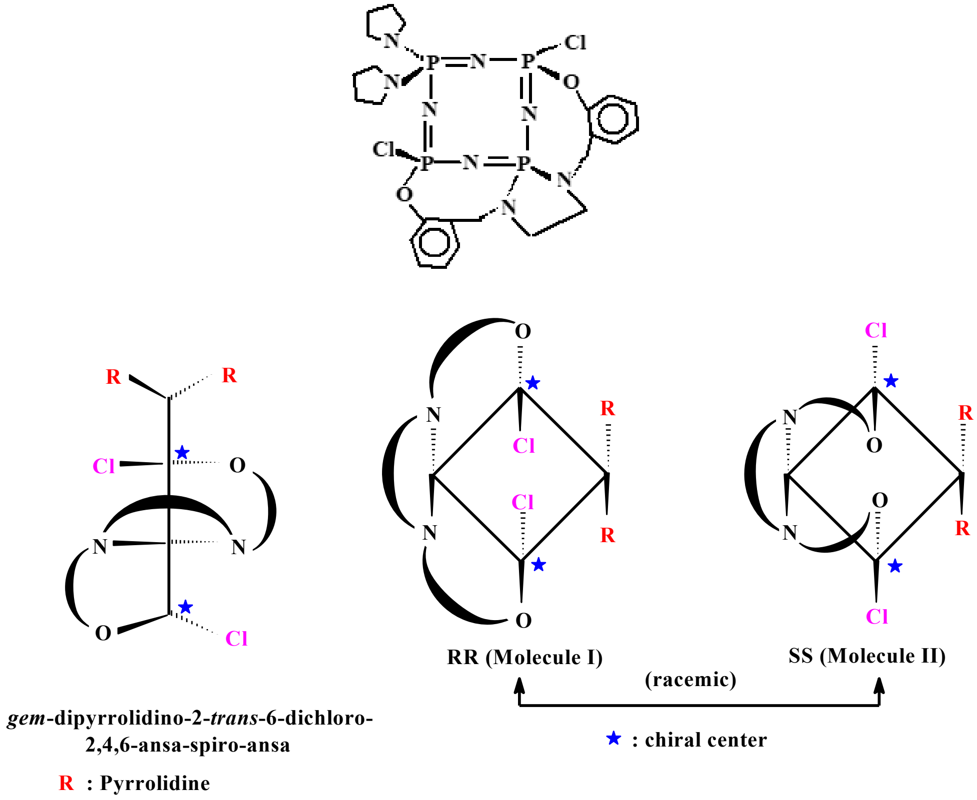


FIGURE 1. Chemical diagram and the racemic forms of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** cyclotetraphosphazene.based on the ORTEP diagram *via* stick diagrams and spatial views.

The molecular structure of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** along with the atom-numbering scheme illustrated in Fig. 2. The conformations of the tetrameric phosphazene rings depicted using the torsion angles of the ring bonds (Table 2). In both molecules, the tricyclic parts are consisted of three eight-membered rings, which are not planar having the total puckering amplitudes, Q_T (Q'_T) [25], of 1.2071(25) Å (for tetramer ring of molecule I with unprimed atoms, Fig 3a), 1.1395(27) Å [for ansa (P1/N1/P2/N5/O1/C1/C6/C7) ring of molecule I] and 1.1317(28) Å [for ansa (P2/N2/P3/N6/O2/C10/C11/C16) ring of molecule I], 1.2457(40) Å (for tetramer ring of molecule II with unprimed atoms, Fig 4a), 1.1675(27) Å [for ansa (P1′/N1′/P2′/N5′/O1′/C1′/C6′/C7′) ring of molecule II] and 1.2843(26) Å [for ansa (P2′/N2′/P3′/N6′/O2′/C10′/C11′/C16′) ring of molecule II] (Figs.3c and 4c). Besides, the five-membered spiro rings of molecule I (P2/N5/N6/C8/C9) and molecule II (P2′/N5′/N6′/C8′/C9′) are in twisted conformations (Figs. 3b and 4b). As expected, the solvent molecule, cyclohexane, is in the chair conformation with an inversion centre.

The endocyclic P—N bond lengths of tetrameric N_4P_4 rings range from 1.547(2) to 1.606(2) Å (for molecule I) and 1.548(2) to 1.605(2) Å (for molecule II). The average endocyclic P—N bond lengths are also 1.581(2) and 1.579(2) Å for molecules I and II, respectively, and they show double bond character. These values are shorter than the average exocyclic P—N bond lengths of 1.645(2) Å (for molecule I) and 1.649(2) Å (for molecule II) (Table 2), and they are around the lower limit of the single bond length. The P—N single and double bonds are generally in the ranges of 1.628-1.691 Å and 1.571-1.604 Å, respectively, in the cyclophosphazene derivatives [26], and the obtained values of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** are in agreement with these values.

Furthermore, the endocyclic P—N—P bond angles of molecules I and II are in the ranges of 125.30(2)-133.44(15)° and 127.39(15)-132.24(15)°, respectively. The average values are found to be as 128.38(15)° (for molecule I) and 128.98(15)° (for molecule II). The P—N—P bond angles have spread, and the similar enlargements of these angles were seen in some cyclophosphazenes in the literature [27]. The endocyclic N—P—N bond angles range from 113.54(11) to 125.73(11)° (for molecule I) and 113.79(11) to 125.38(11)° (for molecule II). The average values are calculated as 119.87(11)° (for molecule I) and 119.99(11)° (for molecule II) as well. These variations in the endocyclic P—N—P and N—P—N bond angles of molecules I and II can reflect the steric hindrances of the bulky N_2O_2 tetradentate ligand and may attribute to the negative hyperconjugation [28,29].

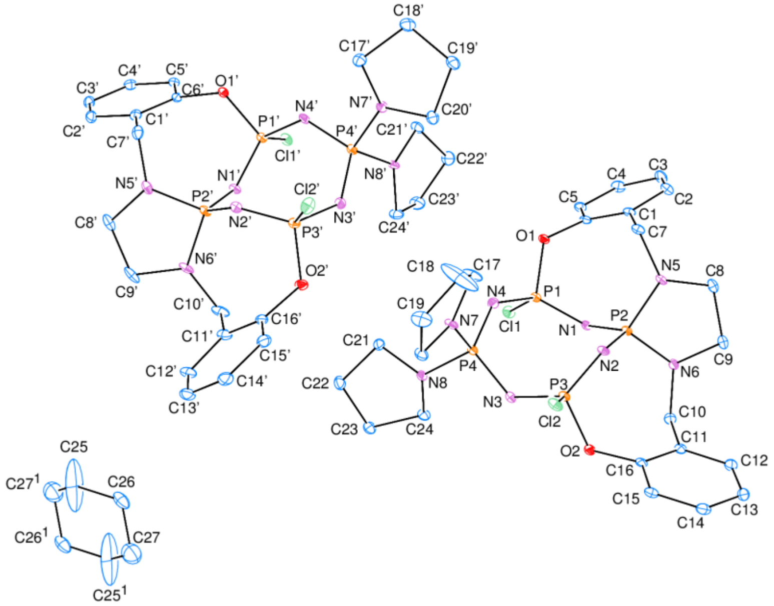
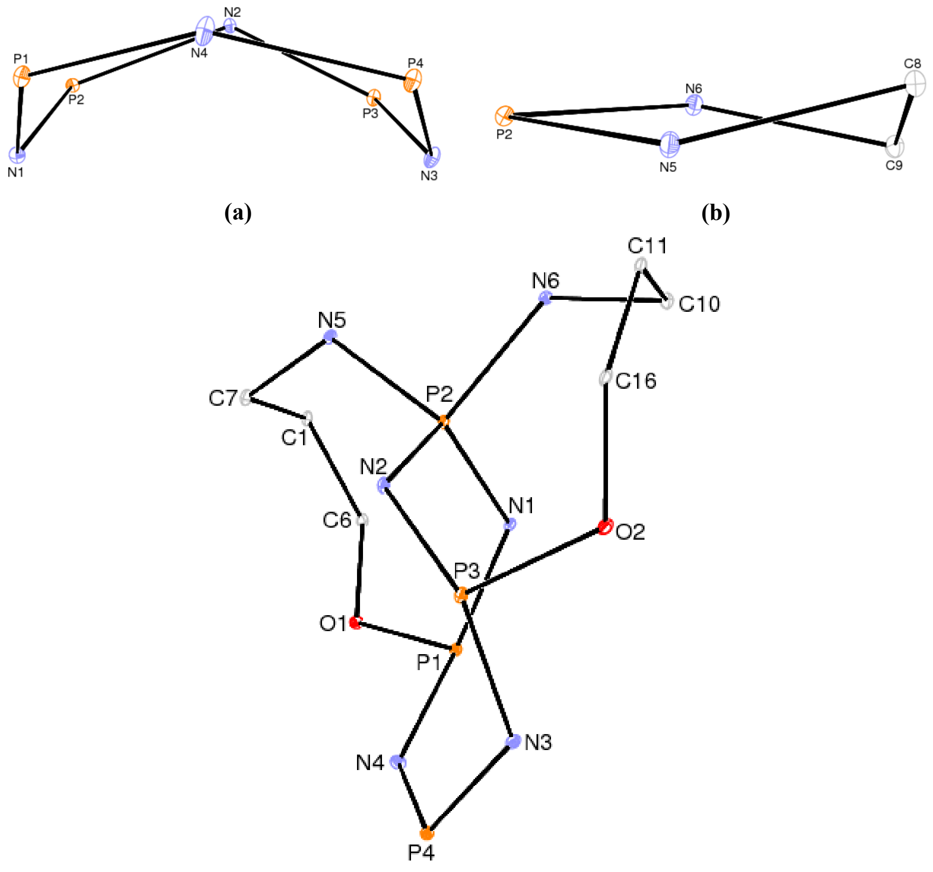


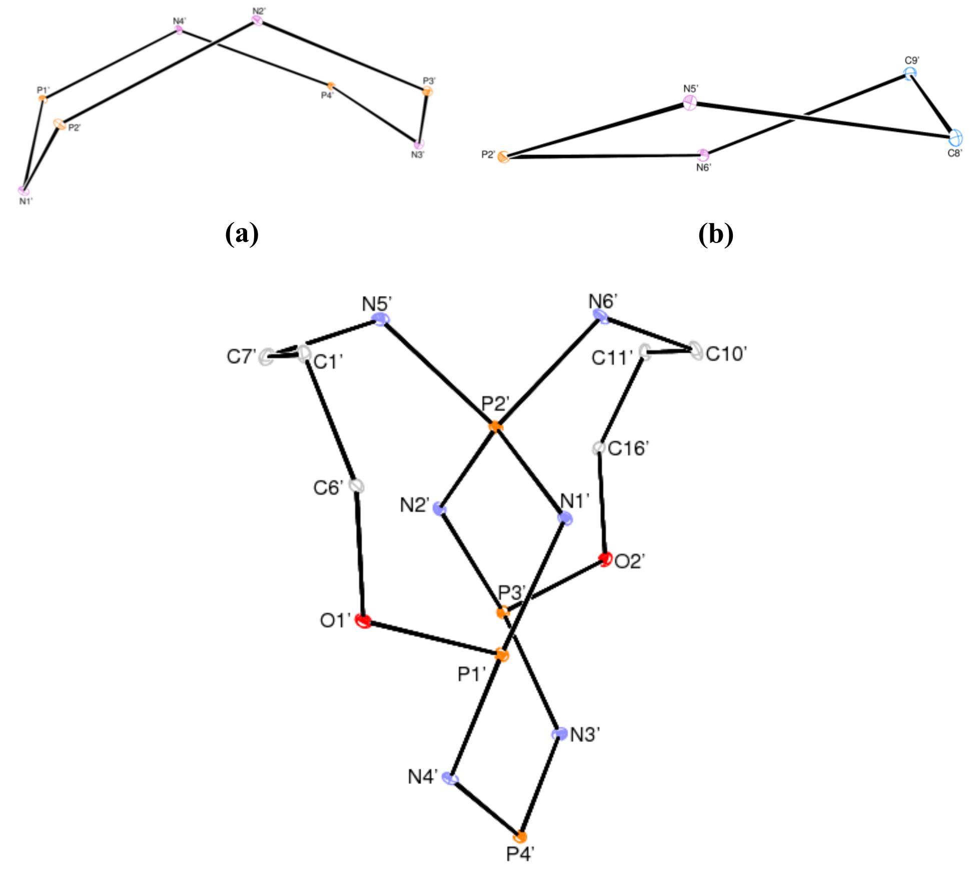
FIGURE 2. An ORTEP-3 [30] drawing of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code 1: -x, -y, -z].



(a) **(b)**

(c)

FIGURE 3. The conformations of (**a**) the tetramer ring, (**b**) the five-membered spiro-ring and (**c**) the all rings of molecule I.



(a) **(b)**

(c)

FIGURE 4. The conformations of (**a**) the tetramer ring, (**b**) the five-membered spiro-ring and (**c**) the all rings of molecule II.

The packing diagram of the ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** compound is depicted in Fig. 5. The molecules are elongated along the c-axis direction and stacked along the a-axis direction. Cyclohexane molecules are located in the intermolecular spaces. It can be considered that Van der Waals interactions are effective in molecular packing, and especially in keeping the guest cyclohexane molecules in the inner holes.

The crystallographic data of the compound has been deposited with the Cambridge Crystallographic Data Centre, CCDC 1953256.

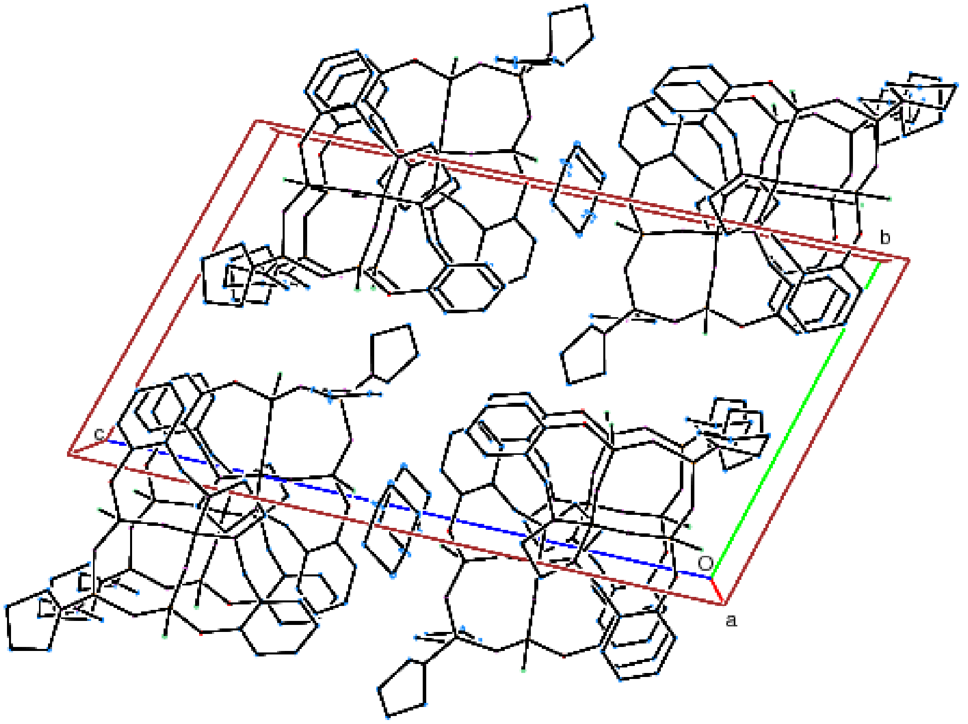


FIGURE 5. The partial packing diagram of ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** compound.

4. Conclusion

In the current paper, the structure of the title ***gem*-dipyrrolidino-2-*trans*-6-dichloro-asa** cyclotetraphosphazene was confirmed by X-ray crystallography. It has two crystallographically independent molecules and one half of the cyclohexane solvent molecule in the asymmetric unit. Both molecules have two equivalent chiral phosphorus (P1 and P3/P1′

and P3′) centres according to X-ray crystallographic data. Moreover, these molecules are in the racemic forms on account of the *trans* manner of the two Cl atoms. It is clearly determined that the absolute configurations of P1, P3 and P1′, P3′ atoms are RR and SS, respectively.

Additionally, the pyrrolidine substituted **asa** tetrameric phosphazene may have important applications in many fields, eg. chemistry, material science, biology and medicine. For example, it can be useful for the preparation of the new chiral products, as ligating agents for the metal cations and as biologically active agents.

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ÖZET

Bir siklotetrafosfazen türevi olan 9,13-dikloro-22,22-dipirolidin-1-il-1*H*,2*H*,13*H*,19*H*-9,13-(epiazenofosfazeno)-9λ^5,11λ^5,13λ^5-[1,3,5,2,4]benzoksadiazadifosfinino[4',5':2,3][1,3,2] diazafosfolo [2,1-*d*] [1,3,5,2,4]benzoksadiazadifosfin, 2($C_{24}H_{32}Cl_2N_8O_2P_4$). 0.5 C_6H_{12} bileşiği, bir tetramerik N_4P_4 ve iki ansa halkası içeren üç sekiz üyeli halkadan oluşan trisiklik yapıdaki *geminal*-dipirolidino-2-*trans*-6-dikloro-*ansa-spiro-ansa* (***gem*-dipirolidino-2-*trans*-6-dikloro-asa**) yapısına sahiptir. Bununla birlikte, tüm bu halkalar düzlemsel değildir. Asimetrik birimde kristallografik açıdan iki bağımsız fosfazen molekülü ve yarım molekül siklohekzan çözücüsü içerir. Her iki molekülde, iki P (P1 and P3/P1′ and P3′) atomlarının stereojenik merkez olması beklenmektedir. Her iki ***gem*-dipirolidino-2-*trans*-6-dikloro-asa** molekülü Cl atomlarına göre *trans* yapıya sahiptir ve rasemik karışım halindedir. Ayrıca, P1, P3 ve P1′, P3 fosfor merkezlerinin mutlak konfigürasyonlarının sırasıyla RR ve SS olduğu bulunmuştur. Uzay grubu, hücre parametreleri a = 9.6682(2), b = 13.8587(3), c = 24.0250(4)Å, $\alpha = 105.249(2)°$, $\beta = 96.298(3)°$ ve $\gamma = 98.367(3)°$ olan *P-1* olup Sohncke uzay grupları arasındadır.

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