Investigation the role of 2-amino pyridine and ET_3N in the substitution and hydrolysis mechanism of the $P_3N_3Cl_6$ by ^{31}P-NMR.

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Abstract

1,3,3,5,5, penta chloro-1- mono (2-amido pyridine) cyclo tri phosphazen and 1,3,5 tri chloro-1,3,5 tri (2-amidopyridine)cyclo tri phosphazen were synthesized by the reaction of trimer with 2-aminopyridine in mole ratio1:1 and 1:3 in aceton by -80^{0}C in Liquid nitrogen bath. The hydrolysis of trimer by the effect of lone pair electron in the nitrogen atom of the 2-amidopyridine was studied by the FTIR and ^1H , ^{13}C , ^{31}P- NMR spectroscopy .

Hexachlorocyclotriphosphazene is found to be stable in $CDCl_3$ and C6D6 in presence of water even at elevates temp. 55^0 c for $CDCl_3$ and 65^{0}c forC_6D_6 duo to time factor it could be stayed stable for more than two week. Only upon addition of ET_3N than hydrolysis is observed, the hydrolysis of trimer with the triethylamine discussed by ^{31}P-NMR spectroscopy.

Keyword: Mechanism , substitution , hydrolysis , Hexachlorocyclotriphosphazene , ^{31}P-NMR

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مناقشة دور 2- امينوبايريدين و ثلاثي اثيل أمين في ميكانيكية الاستبدال والتحلل المائي لسداسي كلورو ثلاثي الفوسفازين- الحلقي بواسطة تقنية الرنين النووي المغناطيسي للفسفور 31 .

صفاء عبد الرحمن السامرائي

الملخص

تم تحضير المركبات 1،3،3،5،5 خماسي كلورو -1- مونو(2- امينو بايريدين) ثلاثي الفوسفازين الحلقي من تفاعل الترامير مع ثنائي امينو بايريدين بنسب مولية 1:1 ، 3:1 في الاسيتون عند درجة حرارة – 80°م في النتروجين السائل.
التحلل المائي للترامير بتأثير المزدوج الالكتروني الحر في حلقة البريدين قد درس بواسطة طيف الاشعة تحت الحمراء للمركبين وطيف الرنين النووي المغناطيسي للبروتون والكاربون 13 والفوسفور 31 .
وقد وجد ان سداسي كلورو ثلاثي الفوسفازين الحلقي مستقراً في ثلاثي كلورو مثلين والبنزين بوجود الماء حتى عند رفع درجة الحرارة الى 55°م لثلاثي كلورو مثلين و 65°م للبنزين اضافة الى عامل الوقت حتى أسبوعين بقي المركب مستقراً.
فقط عند اضافة ثلاثي اثيل امين لوحظ التحلل المائي وقد تم دراسة التحلل المائي للترايمر مع ثلاثي اثيل امين بواسطة طيف الرنين النووي المغناطيسي للفوسفور 31 .

كلمات مفتاحية: الالية ، الاستبدال ، التحلل المائي ، سداسي كلوروثلاثي الفوسفازين الحلقي ، فوسفور 31

Introduction

Phosphazenes , compound having –P= N– group in their molecules , constitute on of the important class of compounds in the chemistry of phosphorus and nitrogen (Fig 1) .

First hetro cyclic compound of the composition $(PNCl_2)_3$ and $(PNCl_2)_4$ were isolated in the 1830 (s) [1-3] from the reaction of PCl_5 with NH_4Cl . since that time, a diverse class of phosphazen ring and linear species has been investigated [4-7] .Hexa chloro-cyclo-triphosphazene , $P_3 N_3 Cl_6$, being easily prepared, is commonly used as a starting materials for many substitutions [8] .

The reaction of hexachloro cycle – triphosphazen (1) with nongeminal(mono substituted) phosphazen derivatives, Dimethyl Amin, monomethylamin ,diethyl Amin, mononaphthaylamin, in mole ratio 1-3 were studied [9-11] . And non geminal substituted

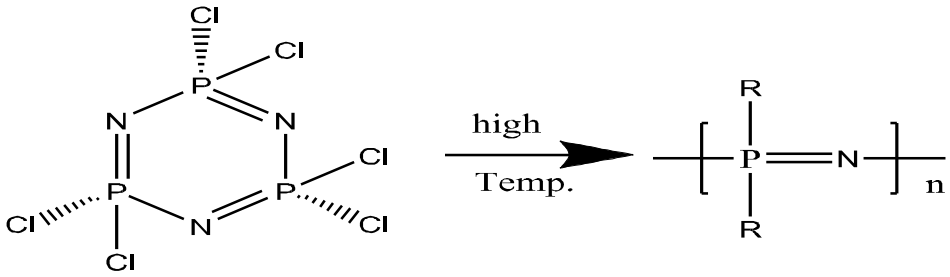
phosphazen derivatives within the context of biological and pharmacological properties of some amido and aminophosphazenes nucleophilic substitution types . in course of these reaction , alone electron per of the reagent(amido) nitrogen atom attacks a phosphorus atom of the phosphazen cycle , and amido or amino – cyclo – tri phosphazen derivatives are formed under release of HCl [12,13] .

The water-soluble mono, poly(aminoaryloxy-methylamino phosphazene) has been synthesized and investigated as monomeric and a polymeric carrier species for the covalent attachment of biologically active agents , and as hydrolytic stable fire-retardant agents .A wide range of phosphazene derivatives were prepared and reported with amino, carbonyl groups, and other functional groups [14,15].

Different side groups grafted on the cyclic phosphazene polymeric backbone generate materials with different features. Their characteristics may vary from those of elastomers to glasses, from water-soluble to hydrophobic polymers, from bio inert to bioactive materials, and from electrical insulators to conductors [16,17,18].

The hydrolysis of chlorophosphpazen cyclic trimer has long been of interest because of its possible relevance to polymerization catalysis , as well as the undesirable role of water in the cross-linking of poly (dichlorophosphazene) the hydroxo tetra chloro cyclo tri phosphazene cyclo- $N_3P_3Cl_4(OH)_2$ and Hexahyroxocyclo-tri-phosphazene (trimetaphosphimic acid) cyclo – $[NH(OH)_2]_3$ intautomeric equilibrium with cyclo- $[HNO(O)(OH)]_3$ has been reported [19-a,19-b]. At low concentration water either acts as polymerization catalyst or reacts with the trimer to generate the active catalytic species .

At water contents greater than 1mol% on insoluble cross linked polymer is formed ,which cannot be derivatized to form useful materials. Allcock and co-worker [20] have proposed that water catalyzes the polymerization in directly by the formation of hydrolyzed trimer species , some of them have been identified by ^{31}p-NMR spectroscopy [21].



(Fig. 1)

Experimental

2.1 : ^{13}C-NMR, ^{1}H-NMR , ^{31}P-NMR spectra were recorded using a Bruker AVANCE III 500MHZ NMR spectrometer . FT-IR spectra was measured by 2000 PERKIN ELMER in KBr disk containing 1.2–1.7 mg of the sample and 100 mg KBr. The melting point measurement was by using GALLEN KAMP apparatus (LABS. USM. uni. MALAYSIA).

2.2 : Materials reagents:

All experimental manipulation were performed under an atmosphere of dry nitrogen . Hexachlorocyclotriphosphazen (mp 120^0c) (cross organic) 98% was obtained after fractional vacuum sublimations at 0.5 torr .

2-aminopyridine (cross organic).

Acetone(D_3COD_3) (Sigma Aldrich) .

Triethyleamin(MEREK) freshly distilled under nitrogen from sodium benzophenon ketyl.

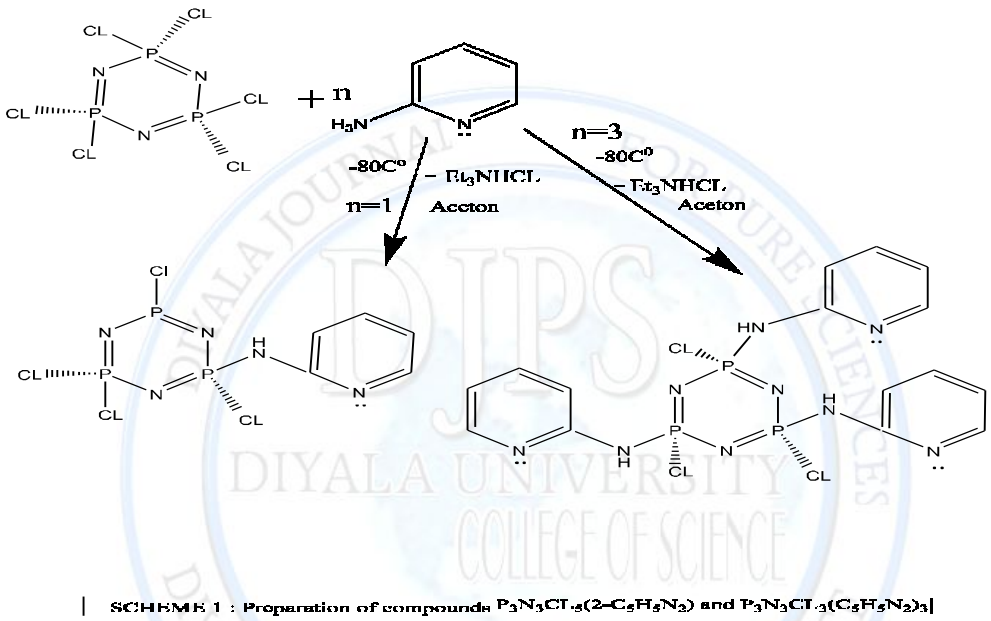
Benzene C_6D_6 (cross organic).)

Chloroform $CDCL_3$ – D1 99.8% (MEREK).

2.3 : Experimental proch :

2.3.1: Hexachlorocyclo-tri-phosphazene was reacted with 2-aminopyridine in Acetone at -80^0C in mole ratio (1:1)and(1:3) with Et_3N (Table 1) in liquid nitrogen bath with acetone , however the reactions were carried out in anhydrous condition for more than(5 h),the triethylamoniumchlorid was filtered off and the solvent reduced to the minimum . the yield of

the products after deep temperature umcrystalization was about 85% for 1,3,3,5,5 penta chloro 1mono(2-amidopyridin)cyclo tri-phosphazen and 77%for 1,3,5 tri chloro-1,3,5 tri(2-amidopyridyin)cyclo-tri-phosphazen,The products were incubated for one month in deep freeze {scheme 1,2}.



SCHEME 1 : Preparation of compounds $P_3N_3CL_5(2\text{-}C_5H_5N_2)$ and $P_3N_3CL_3(C_5H_5N_2)_3$

Table (1): amount of reactants and solvents used in the prepared compounds :

Synthesized compound	$P_3N_3CL_6$(g/mol)	legend reagent(g/mol) / Et_3N mol	solvent(cm^3)	Ratio
1	0.5/0.001	2-aminopyridine / 0.001 0.25/0.002	Aceton(25)	1:1
2	1.5/0.003	2-aminopyridine / 0.003 0.75/0.006	Aceton(50)	1:3

2.3.2 : (40 mg) from trimer has been dissolved in duterated chloroform and measured in ^{31}p-NMR as a standard [Fig2-a] .

The purity of chloroform was confirmed through ^{1}H-NMR spectrum [Fig2-b].

The trimer solution incubated for more than one week after addition of one drop of distill water The experiment has repeated by using Benzene to know the effectiveness on the trimer , the solution has incubated for one week.

The same steps has repeated by changing the temperature, were the temperature has increased from 25 ^{0}C to 35 ^{0}C gradually , then to 55 ^{0}C with chloroform and 65 ^{0}C with Benzene[Fig3 - a].

After addition one drop of triethylamin, the reaction occur after 10 minute from the addition , it has observed on the ^{31}p-NMR [Fig4,5,6].

The same experiment has repeated with solution of trimer dissolved in benzene [Fig3-b

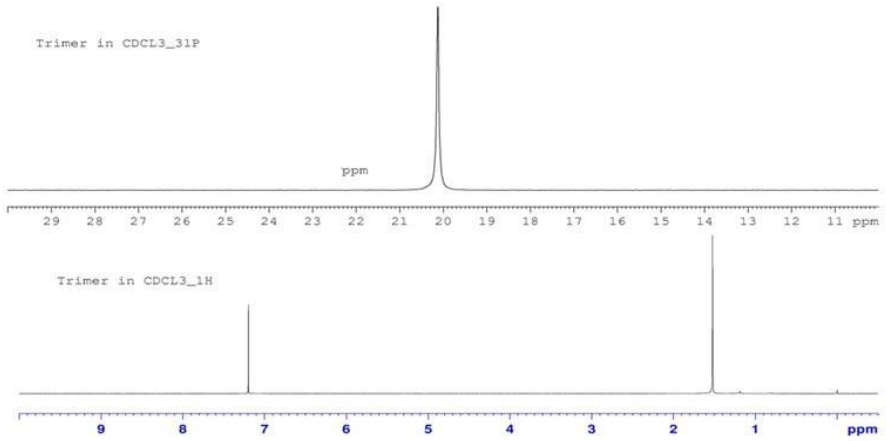


Fig (2-a) : the ^{31}P – NMR signal for the trimer after two weeks incubated in chloroform

Fig(2-b) : ^{1}H-NMR signal for the trimer after two weeks in chloroform

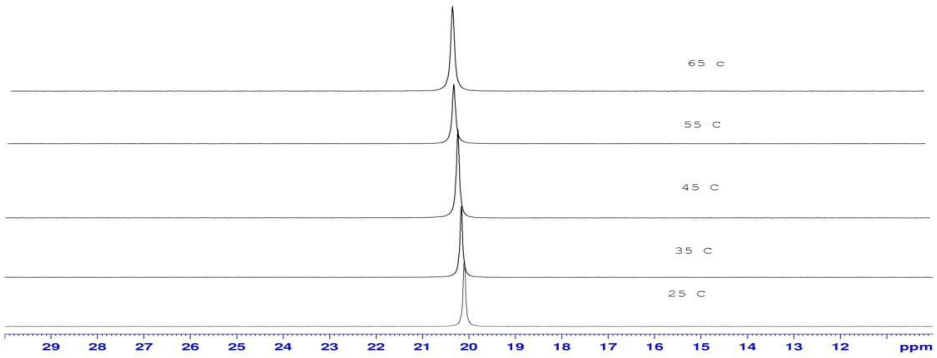


Fig (3-a) : the purity of trimer in benzene with deferent temperature degrees.

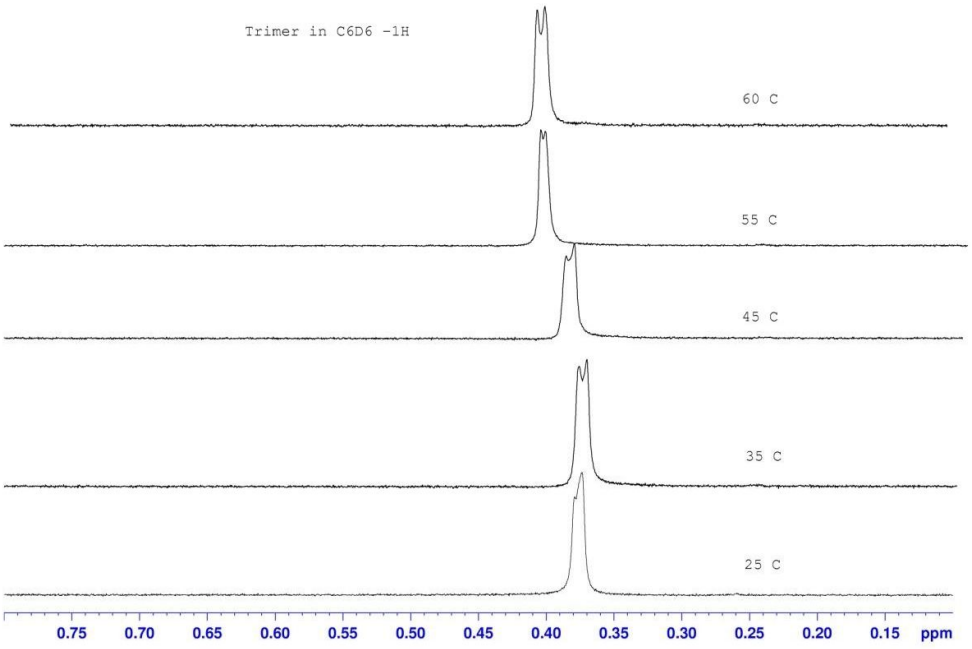


Fig3-b) : ^1H –NMR for benzene in variable temperatures)

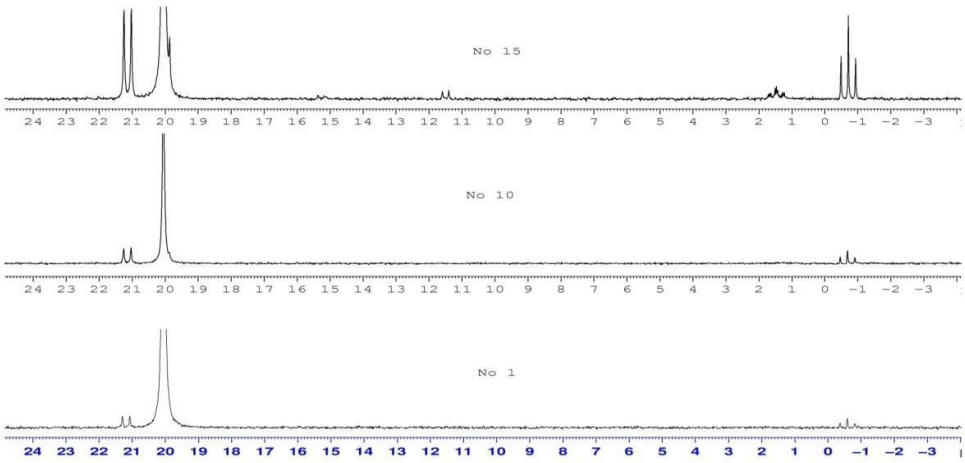


Fig.4: (Exp.no:1,10,15) The^{31}P-NMR hydrolysis results of the compound [P3N3Cl4(OOH]

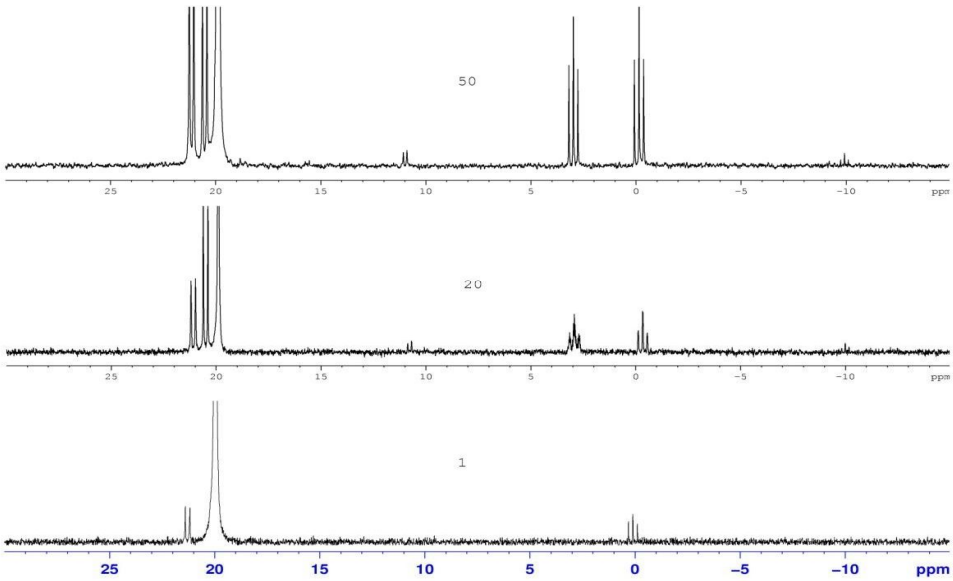


Fig.(5) :(Exp.no: 1,20,50) The^{31}P-NMR hydrolysis results of the compound [P3N3Cl4(OOH)].

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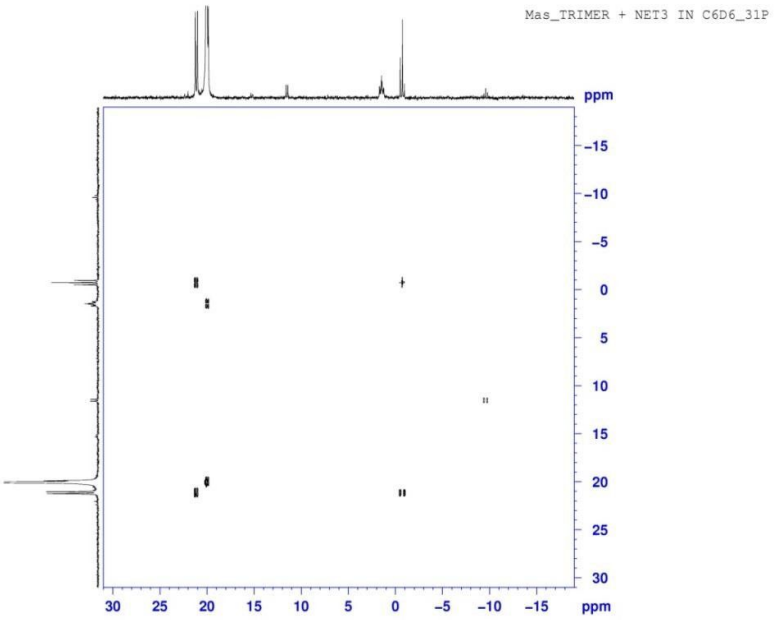


Fig.(6)The Possible stereoisomer structure of compound

At ambient temperature in CD_6C_6

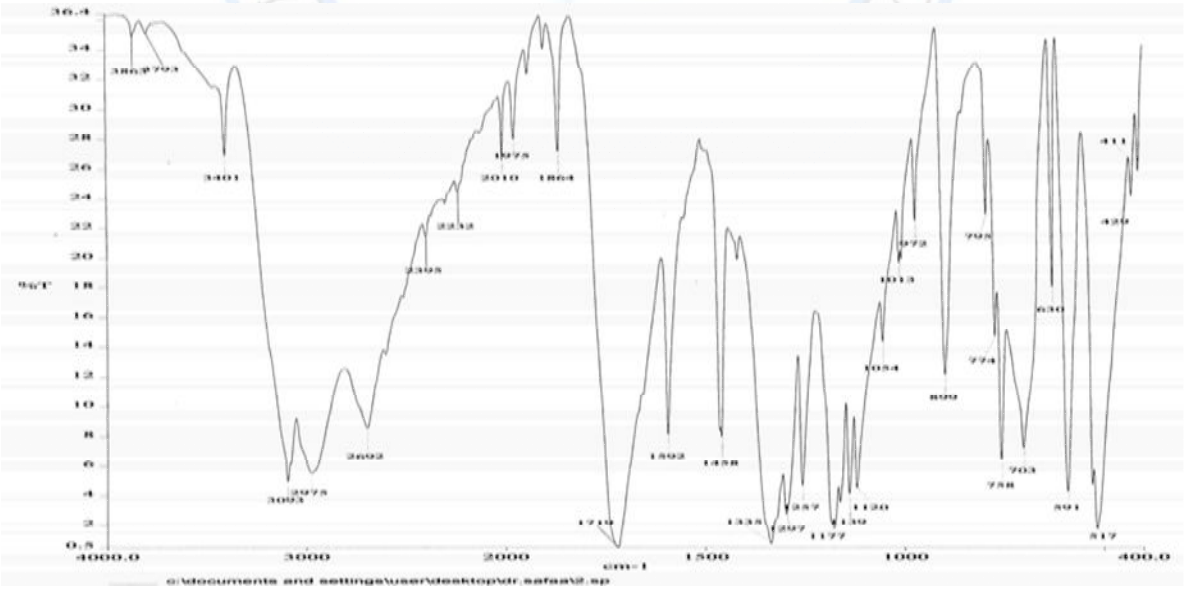
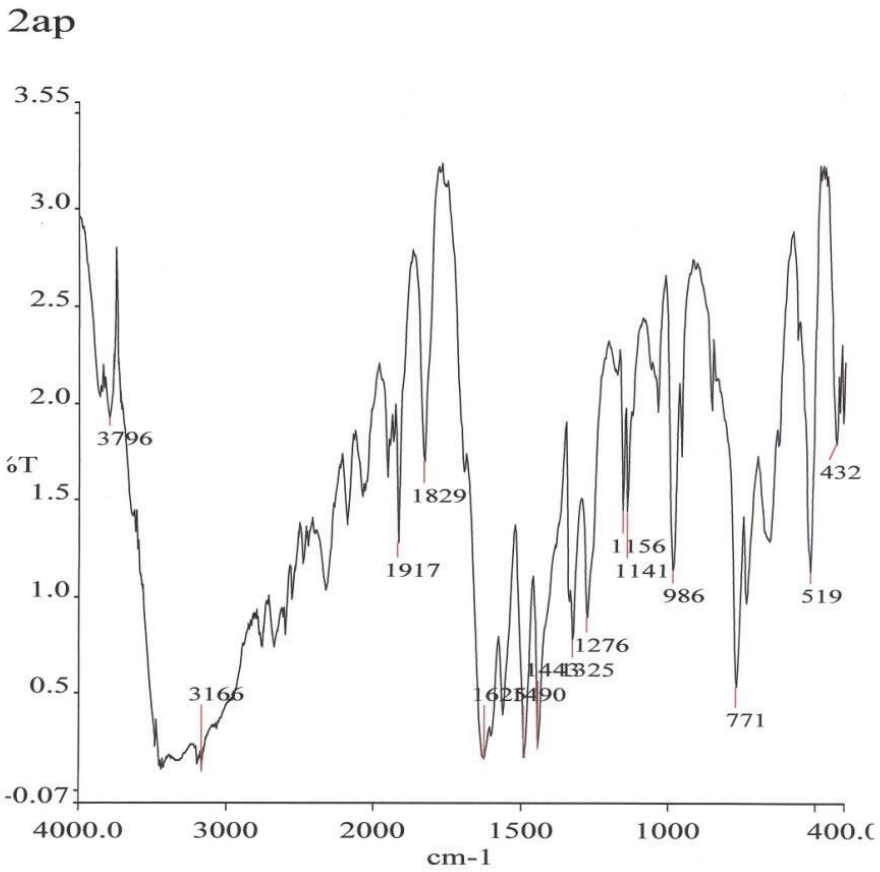


Fig.(7): FTIR for the 2-aminopyridine



(Fig.8): FTIR for the trimer with 2-aminopyridine(2-ap).

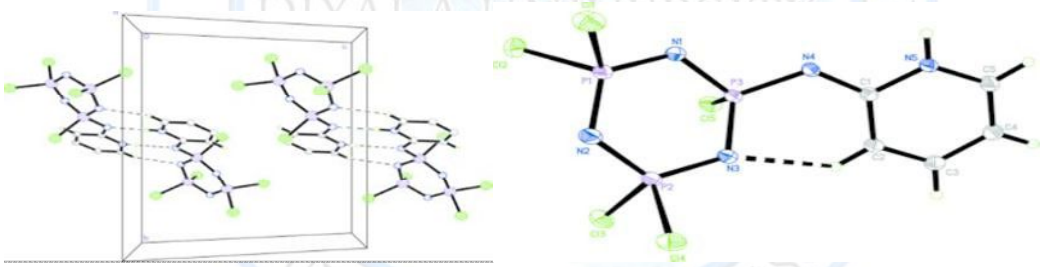
Results and conclusion

The FT-IR data (table 2) shows the presence of the C-N and P-N groups vibrations. The weak signal for the NH vibration in the prepared compound is shifted to lower frequency by (5–8) cm-1. The decreasing of the P=N frequency is due to the weakening of the phosphazene skeleton bond as a consequence of the chlorine replacement with NH_2 moiety

Table(2) : FT-IR data for the prepared compound in cm^{-1}:

compound	N-H str	C-H	C-N	C=C	P=N	P-N
$P_3N_3Cl_{5(2\text{-}AP)}$	2411	2739	1554	850	1141	906
$C_5H_6N_2$	3441	2761	1561	855	-	-

The structure of the white crystals of the compound 1,3,3,5,5, penta chloro –1 mono (2-amido pyridine) cyclo tri phosphazen was proven by the X-ray diffraction[22][fig.9] and supported by the FTIR and 1H, ^{13}C, ^{31}P-NMR spectroscopy The structure of the compound was elucidated by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. There are two peaks in the ^{31}P NMR spectra with similar Jp-p values 41.88 and 45.98(d,t) that show that the compound have one isomer. The ^{1}H and ^{13}C NMR data also confirm the structure of the compound (Table5) .



[Fig.9]

pyridin-2-yl-amine} -Pentachloro-2λ5,4λ5,6λ5-[1,3,5,2,4,6]triazatriphosphinin-2- yl-(2,4,4,6,6 {

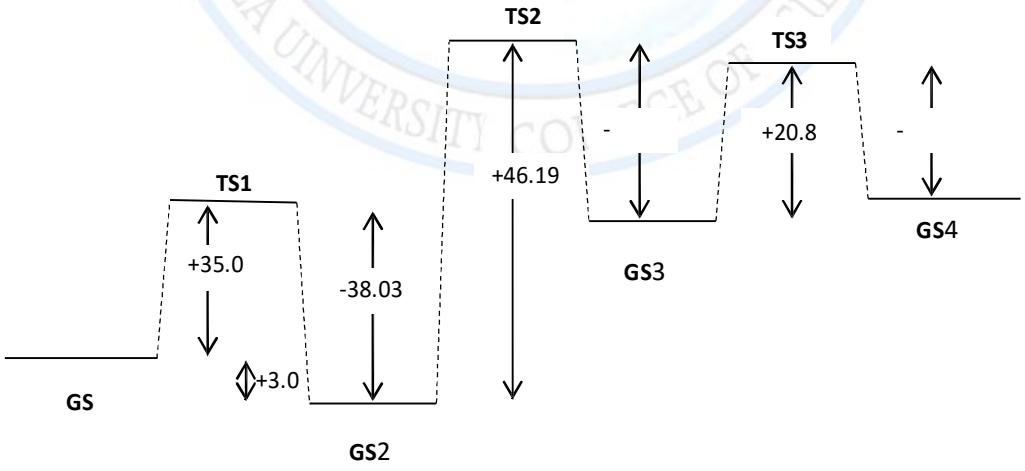
The optimized molecular structures, relative stability and vibrational frequencies were investigated by using ab initio density functional theory (B3LYP), with basis sets{ 6-311G++(d,p)} [23].

Thermodynamic parameters

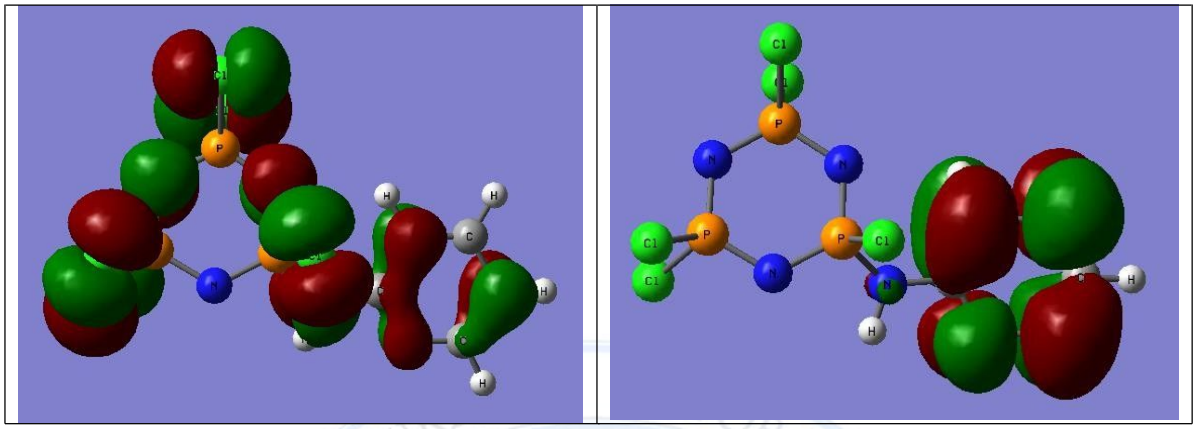
[Table 4]: shows the total electronic and zero-point energies (ZPE) and other thermodynamic parameters of the 1,3,3,5,5-penta chloro-1-mono (2-amidopyridin) cyclo triphosphazen and its tautomers structures in the GSs and TSs. Results show that the energies in the GS increased in the sequence of GS4 > GS3 > GS1 > GS2, while the TS energies are TS2 > TS3 > TS.[Fig.10].

Table 4: Energies of the 1,3,3,5,5-penta chloro-1-mono (2-amidopyridin) cyclo triphosphazen and its tautomers structures

	ZPE	E	G	H
GS1	0.125081	-3792.836517	-3792.762872	-3792.691442
TS1	0.119373	-3792.780663	-3792.713116	-3792.641465
GS2	0.124646	-3792.841350	-3792.767889	-3792.696807
TS2	0.118681	-3792.767747	-3792.700308	-3792.629310
GS3	0.123077	-3792.805257	-3792.735165	-3792.661800
TS3	0.118742	-3792.771977	-3792.704176	-3792.633505
GS4	0.123080	-3792.801657	-3792.730731	-3792.658220



[Fig 10]: Energy profile for the 1,3,3,5,5-penta chloro-1-mono (2-amidopyridin) cyclo triphosphazen and its tautomer structures .



LUMO-HOMO energies

[Fig.11]: shows the distribution of electron density on HOMO and LUMO orbitals and their energies.

The aromatic CH for the pyridine ring appears between 120 and 141 ppm. In the ^1H NMR spectra, the NH proton is observed at 1.72 ppm, which shows according to the e integral intensities that there is one position for the NH proton in the compound.[Table5].

Table (5) : ^{31}P NMR ,^1H, ^{13}C NMR Spectra for prepared compounds :

compound	^{31}P (d)	δd	J_{P-P}(d) HZ	^{31}P (t)	δt	J_{P-P} (t) HZ	^{13}C	^1H NH	J_{P-P} HZ
$P_3N_3CL_5$(2-AP)	19.89 19.57	19.60	41.88	6.87 6.67 6.46	6.66	45.98	120.47 122.12 127.29 129.23 141.25	1.72	44.76 45.33
$P_3N_3Cl_5OH$(2-AP)	21.87 21.56	21.69	26.84	-8.12 -8.31 -8.51	-8.47	24.95			

$P_3N_3CL_3(2\text{-AP})_3$	21.54 21.28 16.56 16.39 16.24 16.04	21.41 16.47 16.14	40.77	7.19 6.94 6.68 0.76 0.64 0.52 0.30 0.16 0.01	6.93 0.64 0.15	44.33		1.75	44.35
$P_3N_3(OH)_3(2\text{-AP})_3$	23.95 23.51 22.67 22.31 19.22 18.79	23.38 22.49 19.00	44.21	1.51 1.41 0.78 -1.45 -1.88 -2.31 -10.26 -10.62 -10.89	0.97 -1.88 -10.25	46.11 44.25			

2-AP = 2- AMIDOPYRIDINE

Table (6) : the ^{31}P NMR data for the trimer hydrolyses in$CDCL_3$:

Exp.no.	Time	Solvent	Signal (d)	$^{\delta}$d	J_{P-P} Hz(d)	Signal (t)	$^{\delta}$t	J_{P-P} Hz(t)
1	10mint.	$CDCL_3$ 25^0C	21.39 21.17	21.28	44.91	0.30 0.09 -0.12	0.09	44.56
5	20mint	=	21.33 21.12 20.70 20.49	21.22 2059	44.70 44.70	3.25 3.03 3.00 0.17 -0.03 -0.25	3.09 -0.15	43.88 39.86
10	30mint	=	21.28 21.06 20.66 20.45	21.17 2055	47.75 39.76	-0.14 -0.16 -0.38 -2.93 -2.95 -2.99	-0.13 -2.95	44.62 38.92

15	10hr	=	20.36 20.42 21.23 21.02 10.94 10.76	20.39 21.12 10.85	44.72 39.90 38.92	2.77 2.73 2.69 2.91 2.86 2.81 -9.76 -9.94 -10.12	2.73 2.86 -9.94	44.43 38.66 39.54
21	12 hr	=	20.60 20.38 21.19 20.97 10.85 10.67	20.49 21.08 10.76	43.55 43.25 36.12	-0.13 -0.35 -0.56 2.79 2.74 2.70 -9.82 -10.00 -10.18	 -0.34 2.74 -10.00	44.68 41.88 38.86
23	16 hr	=	20.59 20.37 21.17 20.95 10.82 10.64	20.48 21.06 10.37	43.38 43.25 35.89	-0.16 -0.38 -0.60 2.69 2.65 2.61 -9.84 -10.02 -10.20	 -0.38 2.65 -10.52	44.72 39.92 38.98
50	18 hr	=	20.61 20.58 21.09 20.90 10.96 10.89	20.59 20.99 10.92	43.81 43.77 37.02	-0.18 -0.27 -0.55 2.66 2.60 2.56 -9.94 -10.90 -10.84	 -0.33 2.60 -10.56	44.76 39.87 39.93
52	19 hr	=	20.58 20.40 21.10 20.89 10.89 10.84	20.49 20.99 10.86	43.60 43.97 35.21	-0.20 -0.16 -0.07 2.20 2.16 2.09 -9.77 -10.73 -10.69	 -0.14 2.15 -10.39	44.66 39.89 38.84

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