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Synthesis and Theoretical Studies of 1,3,3,5,5-Pentachloro-1-mono-(2-amidopyridin)cyclotriphosphazene

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1,3,3,5,5-Pentachloro-1-mono(2-amidopyridine)cyclotriphosphazene was prepared from hexachlorocyclotriphosphazene and 2-amino pyridine in acetone. The structure of the white crystals of the prepared compound was elucidated by the X-ray diffraction and supported by the FTIR and ^{1}H, ^{13}C, ^{31}P NMR spectroscopy. Since the X-ray diffraction is not accurate in detecting the position of the hydrogen atoms, Density functional theory (B3LYP) was used to study the structure and the spectroscopic properties of the compound and its tautomers that belong to the hydrogen tautomerism. Calculations have shown that the isomer in which the hydrogen attached to the nitrogen atom of the amido nitrogen that attached to the pyridine ring has the lowest energy and that comes in accordance with ^{1}H NMR and FTIR spectroscopy. Potential energy curve with calculated activation energy is reported.

Key Words: Triphosphazene, Cyclotriphosphazine, DFT, Tautomerism, Potential energy curve.

INTRODUCTION

Hexachlorocyclotriphosphazene reacts with amino derivatives in different moles ratio to form *geminal* and non-*geminal* amido phosphazene[1,2]. In recent years, phosphazene have attracted considerable attention because they can be tailored to possess a wide variety of physical and chemical properties by changing the side groups[3]. The reactions of hexachloro cyclo triphosphazene, ($N_3P_3Cl_6$), with mono, di, tri and tetra-functional amines have been extensively studied[4-7] and especially large difunctional diamines were reported for a potential value in cancer chemotherapy as selective carriers for delivering anticancer drugs to malignant target cells[8,9]. Within the context of biological and pharmacological properties of some amido- and amino phosphazenes, nucleophilic substitutions (ammonolysis and aminolysis) belong to the two main reaction types. In the course of these reactions, a lone electron pair of the reagent nitrogen atom attacks a phosphorus atom of the phosphazene ring and amido- or amino-cyclotriphosphazene derivatives are formed under release of HCl[10,11]. The result of the reaction of phosphazene derivative with nucleophile reagent strongly depends on reaction conditions whereas a series of various substitution derivatives can be formed[12-18]. The reactions of $N_3P_3Cl_6$ with aromatic primary amines (aniline, *p*-toluidine and *p*-anisidine) as a model systems for the phosphazene have shown that the second stage of chlorine replacement in methyl cyanide (MeCN) proceeds by a bimolecular mechanism[19]. This result implies that the products formed are presumably the non-*geminal bis*-(amino) derivatives. In contrast to the previous report of a predominantly *geminal* mode of substitution established for aniline in benzene[20,21].

In this study, density functional method (DFT) was used to study the tuotomers of the prepared compound. The potential energy curve, spectroscopic and thermodynamic properties are calculated and compared with the experimental results.

EXPERIMENTAL

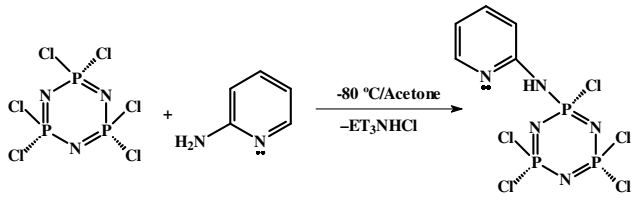
Synthesis procedure and sample preparation were performed under dry nitrogen atmosphere. Pure hexachloro cyclotriphosphazene (cross organic) was obtained from subsequent sublimation in vacuum at 60 ºC. The purity was checked by ^{31}P NMR spectroscopy. 2-Aminopyridine was taken from (Aldrich), triethylamine (Et_3N) was purified according to[22] and distilled before use.

^{31}P NMR spectra was recorded on a 500 MHz BRUKER-TT-AVANCE spectrometer and was referenced to H_3PO_4 85 % (external standard). The sample was dissolved in deuterated aceton. 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 measurment was by using Gallen Kamp apparatus.

TABLE-1
^{31}P, ^{1}H, ^{13}C NMR SPECTRA FOR THE PREPARED COMPOUND

Compound	^{31}P (d)	-d	JP-P(d) HZ	^{31}P (t)	-t	JP-P (t) HZ	^{13}C	1H NH	JP-P HZ
$P_3N_3Cl_5$ (2-AP)	21.87 21.66	21.76	41.88	6.87 6.67 6.46	6.66	45.98		1.72	40.89 45.33
							120.47 122.12 127.29 129.23 141.25		

Hexachlorocyclo-*tri*-phosphazene (0.5 g, 0.07 mol) was reacted with 2-aminopyridine (0.13 g, 0.07 mol) and triethylamine (0.14 g, 0.07 mol) in acetone at -80 ºC in mole ratio 1:1 in liquid nitrogen bath, however this reaction was carried out in anhydrous condition for more than 5 h. The triethylammonium chloride was filtered off under nitrogen air, washed with dried acetone and the solvent reduced to the minimum and 10 mL dried acetone was added. The product yield of 1,3,3,5,5-penta chloro-1-mono-(2-amidopyridine)cyclotriphosphazene after deep freezing crystallization was about 60-66 %, melting point 182 ºC. Crystals suitable for X-ray diffraction studies were obtained after two months of deep freezing uncrystallization and by nitrogen air dried.



Computational methods: The structure of 1,3,3,5,5-pentachloro-1-mono-(2-amidopyridine)cyclotriphosphazene and its tautomers structures were modelled according to the structure proposed by X-ray diffraction[23]. The optimized molecular sturctures, relative stability and vibrational frequencies were investigated by using ab initio density functional theory (B3LYP), with basis sets 6-311G++(d,p). In the ground state (GS), the optimized structures have no imaginary frequencies, meanwhile, in the transition state (TS), only one imaginary frequency is observed. The harmonic frequencies and theoretical infrared and Raman spectra were computed and compared to the experimental data. All of the calculations were done by using Gaussian 03W software[24].

RESULTS AND DISCUSSION

The FT-IR spectra for the prepared compound, $P_3N_3Cl_5$, was compared with the reactant, 2-aminopyridine. The frequencies of the N-H stretching were 3411 and 3441 cm^{-1} respectively. Two frequencies was found in the spectra of $P_3N_3Cl_5$ and not in the spectra 2-aminopyridine and that proves the compound formation. 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.

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. The aromatic CH for the pyridine ring appears between 120 and 141 ppm. In the ^{1}H NMR spectra, the NH proton is observed at 1.72 ppm, which shows according to the integral intensities that there is one position for the NH proton in the compound. Several references had been reported in literature regarding the amido phosphazen, such as methylamine, dimethylamine, ethylamine, piperidine[25,26].

Geometry optimization

Four structures was modeled for the prepared compound as follows; GS1, in which the hydrogen atom is attached to the nitrogen atom of the pyridine ring, GS2, is the structure in which the hydrogen atom is attached to the amido group and GS3 and GS4 in which the hydrogen is attached to the *ortho* and *meta* nitrogen atoms of the triphosphazene ring respectively. In addition, three transition state structures were modeled in which the hydrogen atom is in between the GS1 and GS2, (TS1), GS2 and GS3, (TS2) and GS2 and GS4, (TS3). The optimized structures of 1,3,3,5,5-penta chloro-1-mono (2-amidopyridine) cyclo triphosphazene and its tautomers in the TSs and GSs are illustrated in Fig. 1.

Tables 2 and 3 show the optimized structural parameters at DFT level of calculation for the 1,3,3,5,5-penta chloro-1-mono (2-amidopyridine) cyclo triphosphazen. Results show most of the bond parameters predicted theoretically in the GS2 are comparable to the experimental data. However, the computed C-H and N-H bonds are slightly longer than the experimental data. Also, the 5H-1N-5C and 5C-2N-2P bond angles have 2.7º and 3.8º difference compared to the experimental data, while the rest of the bond angles have not shown significant deviation.

When the molecule at GS1 undergoes a TS (TS1), the 5H atom is observed located between 1N and 2N atoms (Table-2). The 1N-5H bond distance has increased by 0.305 Å and the 1N-5H and 2N-5H bond distances are 1.318 Å and 1.380 Å, respectively. In general, most of the bond distances in the TS1 did not changed significantly as in the GS1. Also, the 4C-5C-1N and 4C-5C-2N bond angles increased 6.6º and 6.7º, respectively in the TS1. The computed activation energy in the TS1 is +35.05 kcal/mol (Fig. 2) with respect to the GS1.

In the GS2, the 5H atom is no longer sharing between 1N and 2N atoms and it is observed to be bonded to 2N atom. The 2N-5H bond distance was observed to be shortened from 1.380 Å in the TS1 to 1.016 Å in the GS2. Next, the bond angles of 4C-5C-2N and 5C-1N-1C are narrowed down 14.4° and 4.6°, respectively, in the GS2. Despite these mentioned parameters,

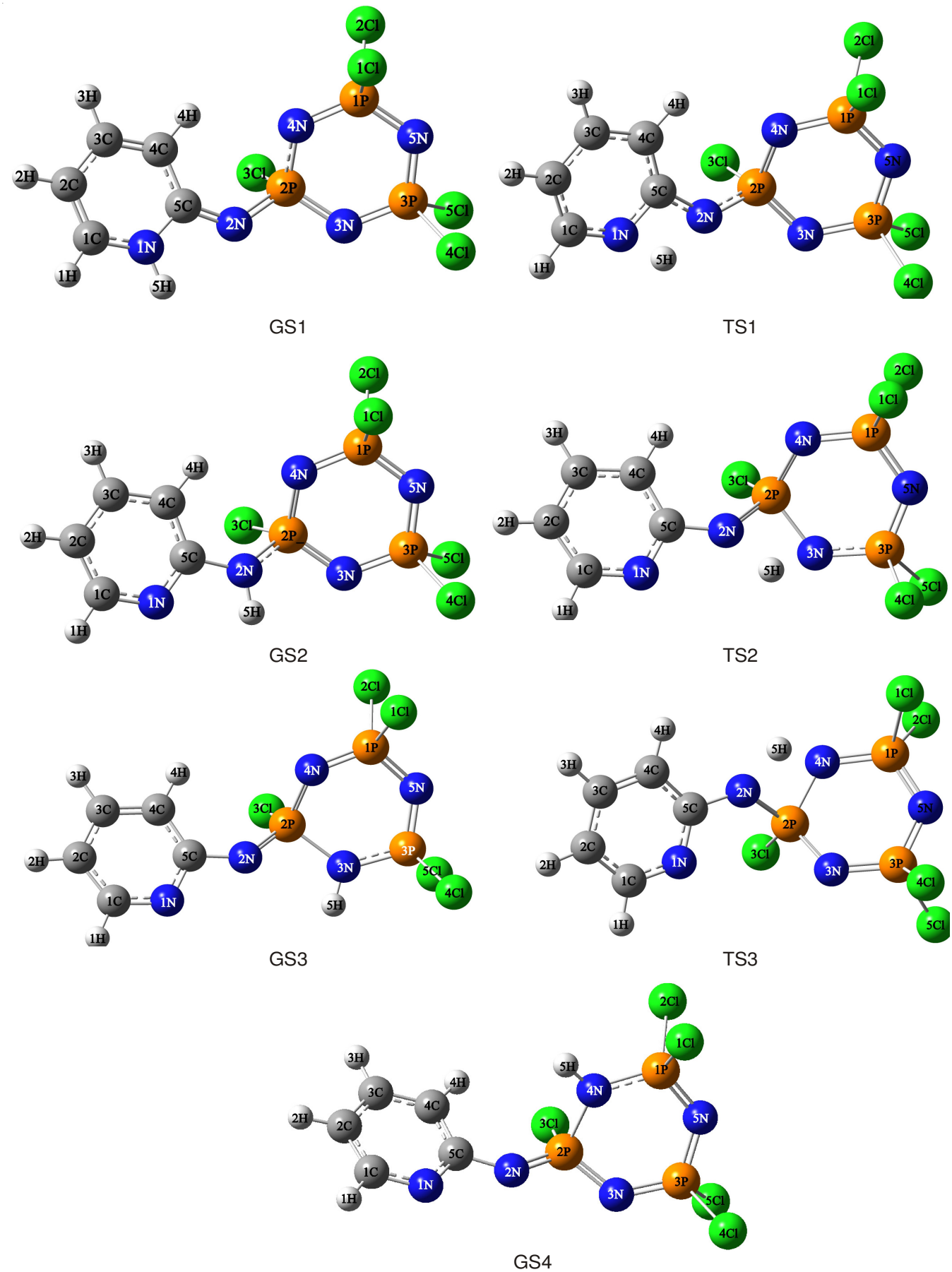


Fig. 1. Atoms numbering and structures of 1,3,3,5,5-penta chloro-1-mono (2-amidopyridine)cyclo triphosphazene and its tautomers structures in the ground state and transition state

TABLE-2
OPTIMIZED STRUCTURAL PARAMETERS OF 1,3,3,5,5-PENTACHLORO-1-MONO(2-AMIDOPYRIDINE) CYCLO TRIPHOSPHAZENE AND ITS TAUTOMERS STRUCTURES CALCULATED AT B3LYP/ 6-311++G(d,p) LEVEL OF THEORY AND THE EXPERIMENTAL DATA

Bond Distance (Å)								
	GS1	TS1	GS2	TS2	GS3	TS3	GS4	Exp.
1C-1H	1.082	1.083	1.086	1.087	1.087	1.086	1.087	0.908
2C-2H	1.080	1.081	1.083	1.083	1.083	1.083	1.083	0.914
3C-3H	1.084	1.084	1.084	1.084	1.085	1.084	1.085	0.951
4C-4H	1.081	1.081	1.082	1.084	1.083	1.083	1.083	0.916
1C-2C	1.363	1.388	1.390	1.391	1.391	1.390	1.392	1.365
1C-1N	1.360	1.335	1.336	1.336	1.335	1.337	1.334	1.357
2C-3C	1.418	1.403	1.394	1.395	1.394	1.397	1.393	1.399
3C-4C	1.369	1.390	1.388	1.386	1.386	1.386	1.387	1.371
4C-5C	1.433	1.397	1.340	1.407	1.409	1.405	1.411	1.421
5C-1N	1.384	1.359	1.332	1.337	1.340	1.339	1.340	1.359
5C-2N	1.313	1.368	1.413	1.392	1.386	1.387	1.384	1.346
1N-5H	1.013	1.318	-	-	-	-	-	0.835
2N-5H	-	1.380	1.016	1.416	-	1.391	-	-
3N-5H	-	-	-	1.271	1.015	-	-	-
2N-2P	1.615	1.627	1.660	1.603	1.529	1.618	1.524	1.597
2P-3Cl	2.099	2.091	2.069	2.060	2.112	2.049	2.115	2.055
2P-3N	1.611	1.607	1.605	1.705	1.749	1.600	1.602	1.603
2P-4N	1.627	1.620	1.607	1.603	1.616	1.712	1.782	1.610
3N-3P	1.583	1.585	1.592	1.622	1.645	1.582	1.569	1.572
4N-1P	1.867	1.620	1.590	1.585	1.571	1.618	1.645	1.571
4N-5H	-	-	-	-	-	1.278	1.014	-
1P-1Cl	2.053	2.051	2.044	2.040	2.035	2.044	2.040	2.015
1P-2Cl	2.055	2.051	2.045	2.040	2.043	2.036	2.037	1.991
1P-5N	1.597	1.597	1.597	1.603	1.616	1.584	1.564	1.586
5N-3P	1.601	1.600	1.597	1.585	1.563	1.605	1.616	1.584
3P-4Cl	1.049	2.047	2.042	2.039	2.037	2.040	2.035	2.001
3P-5Cl	2.052	2.049	2.043	2.034	2.033	2.040	2.039	1.999

the rest of the bond parameters did not deviate drastically from TS1 to GS2. The predicted forward energy in the GS2 is -38.03 kcal/mol (Fig. 2).

Subsequently, in the GS2 the molecule undergoes a TS (TS2), where the 5H atom is moving in between the 2N and 3N atoms (Table-1). The 2N-5H bond distance has increased by 0.4 Å in the TS2 and became 1.416 Å. The 3N-5H bond distance is slightly shorter than the 2N-5H bond distance (1.271 Å). Then, the 5H-2N-5C bond angle has increased 31.8° to 143.8° in the TS1. In general, the rest of the bond parameters in the TS2 did not changed significantly compared to the GS1. The computed activation energy in the TS2 is +46.19 kcal/mol (Fig. 2), which is 11.14 kcal/mol less stable than the reaction in the TS1.

In the forward reaction of TS2 (GS3), the 5H atom is observed to be bonded to 3N atom with a bond distance of 1.015 Å. Next, the bond angles of 5H-3N-2P, 5C-2N-2P and 2P-4N-1P are broaden 35.9º, 2.3º and 3.0º, respectively, in the GS3. With exceptions of these bond parameters, the remaining bond parameters did not have significant changes from TS2 to GS3. The predicted forward energy in the GS3 is -23.54 kcal/mol (Fig. 2), which are 14.49 kcal/mol less exothermic than GS2.

Again, the molecule GS3 the molecule undergoes a TS intermediate (TS3). The 5H atom is moving in between of 2N and 3N atoms (Table-1). The 2N-5H and 4N-5H bond distances in then TS3 are 1.278 Å and 1.391 Å, respectively. The 3N-5H bond distance is slightly shorter than the 2N-5H bond distance (1.271 Å). As a conclusion, all of the bond distances in the TS3 and GS3 are comparable to one another. However, due to the different conformation observed in the TS3 and GS3 (Table-1), the 5C-2N-2P, 2P-4N-1P, 5N-3P-4Cl and 5N-3P-5Cl bond angles are observed to be decreased in the interval of 3º-9º and 5N-3P-3N bond angle increased 4.3º in the TS3. The computed activation energy in the TS3 is +20.88 kcal/mol (Fig. 2), which is kinetically more stable than the TS1 and TS2 by 14.17 and 25.31 kcal/mol, respectively. In the forward reaction (GS4), the 5H atom is found bonded to 4N atom with a bond distance of 1.014 Å and the 5H-4N-2P bond angle has increased 37.5º and became 115.1º. Due to the conformation of molecule changed from TS3 to GS4, the bond angle of 5C-2N-2P has highly broadened 10.8º, while the 2N-2P-3Cl, 2P-4N-1P and 3P-3N-2P bond angles are slightly increased 2.5º, 2.9º and 3.1º, respectively, in the GS4. The predicted forward energy in the GS4 is -18.62 kcal/mol, Fig. 2, which are 19.41 and 4.92 kcal/mol less exothermic than GS2 and GS3.

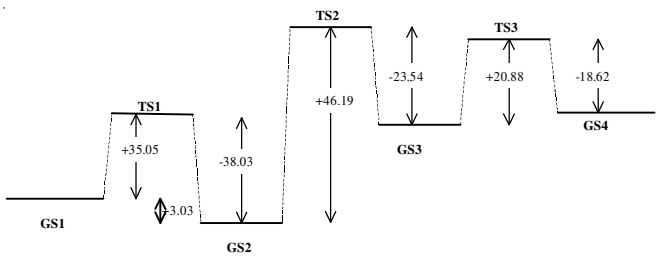


Fig. 2. Energy profile for the 1,3,3,5,5-penta chloro-1-mono (2-amido-pyridine) cyclo triphosphazene and its tautomers structures

TABLE-3
OPTIMIZED BOND ANGLES OF 1,3,3,5,5-PENTACHLORO-1-MONO-(2-AMIDOPYRIDINE)CYCLO TRIPHOSPHAZENE AND ITS TAUTOMERS STRUCTURES CALCULATED AT B3LYP/6-311++G(d,p) LEVEL OF THEORY AND THE EXPERIMENTAL DATA

Bond Angle (º)								
	GS1	TS1	GS2	TS2	GS3	TS3	GS4	Exp.
1H-1C-2C	123.9	123.1	120.9	120.4	120.3	120.7	120.3	123.6
1C-2C-2H	120.4	120.1	120.5	120.7	120.7	120.6	120.8	119.7
2H-2C-3C	121.8	121.1	121.6	121.6	121.7	121.6	121.8	122.2
2C-3C-3H	119.3	119.3	120.6	120.7	120.8	120.5	120.8	120.1
3H-3C-4C	119.1	119.1	119.7	120.0	120.0	120.0	120.0	119.1
3C-4C-4H	121.6	123.0	121.6	120.8	120.9	121.8	120.4	120.1
4H-4C-5C	117.8	120.7	120.9	120.7	120.2	120.1	120.5	119.4
4C-5C-1N	114.7	121.3	123.7	122.6	122.0	122.8	121.7	116.2
4C-5C-2N	130.3	137.0	122.6	122.4	122.7	120.0	123.2	128.0
5H-1N-5C	114.5	78.8	-	-	-	-	-	117.2
5H-1N-1C	120.4	158.8	-	-	-	-	-	119.0
5H-2N-5C	-	-	112.0	143.8	-	150.9	-	-
5H-2N-2P	-	-	-	-	-	78.1	-	-
5H-3N-2P	-	-	-	77.4	113.3	-	-	-
5H-3N-3P	-	-	-	136.7	120.5	-	-	-
5H-4N-2P	-	-	-	-	-	77.6	115.1	-
1N-5H-2N	-	103.1	-	-	-	-	-	-
1H-C1-1N	116.0	117.3	115.7	115.6	115.6	115.7	115.5	115.7
1N-C1-C2	120.1	119.6	123.4	124.0	124.2	123.6	124.2	120.6
1C-2C-3C	117.9	118.7	117.9	117.7	117.6	117.8	117.5	118.1
2C-3C-4C	121.6	121.7	119.7	119.3	119.2	119.5	119.3	120.8
3C-4C-5C	120.6	116.4	117.5	118.5	118.9	118.1	119.0	120.4
5C-1N-1C	125.2	122.4	117.8	117.9	118.1	118.1	118.3	123.8
5C-2N-2P	127.3	129.2	129.03	134.7	137.0	128.3	139.1	123.5
2N-2P-3Cl	105.1	106.0	106.0	112.6	114.3	113.6	116.1	106.7
2P-4N-1P	122.7	122.0	122.1	124.4	127.4	122.9	125.8	120.1
4N-1P-5N	118.2	118.1	118.1	117.2	116.3	115.7	112.7	119.1
4N-1P-1Cl	108.5	108.5	108.9	109.2	109.5	107.3	106.8	111.1
4N-1P-2Cl	110.7	110.6	110.0	110.8	113.2	110.7	111.0	108.3
1P-5N-3P	121.2	122.0	122.7	124.8	125.3	124.3	125.2	118.5
5N-3P-4Cl	108.7	108.8	109.2	112.1	113.6	109.2	108.5	108.0
5N-3P-5Cl	107.9	108.1	108.6	108.5	110.7	107.2	106.3	108.4
5N-3P-3N	118.4	118.0	117.6	115.3	113.0	117.3	116.9	120.2
3P-3N-2P	122.9	122.4	122.0	123.0	126.2	124.6	127.7	121.8

Vibrational spectra: The vibrational frequencies and infrared intensities for the optimized geometries of the 1,3,3,5,5-penta chloro-1-mono (2-amidopyridine) cyclo triphosphazene and its tautomers structures in the GSs were investigated using the B3LYP/6-311++G(d,p) method. Vibrational assignments based on these obtained parameters were performed and compared to the experimental data. The vibrational frequencies and infrared intensities are summarized in Table-4.

TABLE-4
VIBRATIONAL ASSIGNMENTS OF 1,3,3,5,5-PENTACHLORO-1-MONO-(2-AMIDOPYRIDINE)CYCLO TRIPHOSPHAZENE AND ITS TAUTOMERS STRUCTURES IN THE GROUND STATES

Frequencies (cm^{-1})					
GS1	GS2	GS3	GS4	Exp	Assignments
3578.9	3546.9	3561.3	3566.2	3411	NH-amido str.
3228.4	3211.3	3195.5	3195.9	---	CH ring str.
3223.1	3200.5	3185.7	3185.8	---	CH ring str.
3211.4	3179.2	3166.7	3165.9	---	CH ring str.
3181.3	3160.2	3141.0	3142.5	3090	CH ring str.
1680.9	1634.3	1622.9	1621.6	---	C-C ring str.
1625.0	1621.0	1601.5	1602.0	1646	C-C ring str.
1581.4	1513.6	1501.4	1504.0	1545	C-N ring str.
1491.5	1474.9	1468.9	1472.6		C-C ring str.
1452.7	1407.9	1431.2	1436.1	1444	NH amido bending
1397.4	1319.6	1324.3	1325.7	---	CH ring bending
1303.3	1312.9	1280.8	1281.9	---	CH ring bending
1245.8	1258.6	1272.9	1280.5	---	CH ring bending
1218.8	1211.0	1258.8	1269.4	---	P-N ring str.
1191.9	1210.0	1205.0	1218.9	---	P-N ring str.
1185.9	1181.8	1176.9	1177.8	1171	CH ring bending
1121.1	1126.9	1149.9	1155.4	---	P-N ring str.
1117.0	1119.1	1115.6	1116.2	---	CH ring bending
1048.9	1072.6	1065.5	1066.3	1036	C-C bending
1035.2	1009.6	1000.8	999.4	---	C-C ring bending
1014.7	1009.1	990.9	994.3	---	CH ring bending
990.0	983.0	973.9	978.0	---	C-C ring bending
950.8	981.4	936.4	924.7	---	CH ring bending
872.2	901.3	875.1	880.5	---	CH ring bending
848.7	869.1	841.4	845.1	---	P-N-P bending
839.5	847.9	801.1	794.5	---	P-N-P bending
785.9	804.8	790.6	791.7	---	P-N-C bending
771.4	792.3	764.5	762.5	771	CH ring bending
766.8	759.5	742.6	747.6	---	CH ring bending
721.1	743.7	710.9	679.0	---	P-N-P bending
715.6	652.1	641.0	640.5	---	C-C-C bending
641.6	640.8	637.5	622.3	---	P-N-P bending
631.3	619.1	590.8	588.6	---	N-H amido bending
582.3	595.0	552.7	550.8	584	N-H amido bending
566.0	571.6	544.6	535.0	---	N-H amido bending

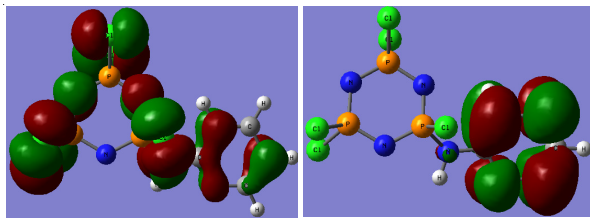
GS1	GS2	GS3	GS4	Exp	Assignments
534.0	544.4	526.1	526.6	---	P-N-P bending
507.5	523.7	510.0	508.2	---	CH ring bending
499.5	507.4	482.1	470.9	---	P-N-P bending
496.8	489.4	471.1	464.9	---	N-H amido bending
468.2	469.7	444.0	434.8	---	P-N-P bending
392.1	420.0	419.1	422.8	---	C-C-C bending
373.3	375.9	374.9	374.2	---	P-N-P bending
340.5	350.6	336.7	337.8	---	P-N-C bending
331.7	332.7	334.0	329.6	---	P-N-P bending
329.6	328.9	319.8	325.2	---	P-N-P bending
319.4	318.6	318.4	303.9	---	P-N-P bending
317.5	312.1	307.4	300.0	---	P-N-P bending
288.5	301.8	284.6	267.6	---	P-N-P bending
271.1	255.8	246.1	263.6	---	P-N-P bending
223.9	222.5	219.5	221.2	---	Cl-P-Cl bending
200.6	202.2	195.2	200.9	---	Cl-P-Cl bending
187.7	195.0	186.4	185.2	---	Cl-P-Cl bending
181.7	181.3	175.2	173.3	---	Cl-P-Cl bending
160.4	163.7	158.7	158.9	---	Cl-P bending
152.8	159.1	151.7	148.4	---	Cl-P-Cl bending
144.2	144.4	135.6	144.0	---	Cl-P-Cl bending
119.2	122.1	111.4	113.7	---	Cl-P-Cl bending
69.8	74.1	55.0	76.2	---	Cl-P-Cl bending
58.3	51.7	41.9	43.7	---	Cl-P-Cl bending
36.2	37.3	38.4	38.0	---	Ring bending
34.9	36.0	27.5	29.9	---	Cl-P-Cl bending
28.6	29.3	17.4	24.0	---	Cl-P-Cl bending
18.8 ()	21.4	16.3	19.6	---	Ring bending

Thermodynamic parameters: Table-5 shows the total electronic and zero-point energies (ZPE) and other thermodynamic parameters of the 1,3,3,5,5-pentachloro-1-mono-(2-amidopyridine)cyclo triphosphazene 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 > TS1.

TABLE-5
ENERGIES OF THE 1,3,3,5,5-PENTACHLORO-1-MONO-(2-AMIDOPYRIDINE)CYCLOTRIPHOSPHAZENE 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

LUMO-HOMO energies: Fig. 3 shows the distribution of electron density on HOMO and LUMO orbitals and their energies.



HOMO = -892.66 kJ/mol LUMO = -540.85 kJ/mol

Fig. 3. HOMO and LUMO orbitals of 1,3,3,5,5-pentachloro-1-mono-(2-amidopyridine)cyclo triphosphazene

REFERENCES

1. Albright and Wilson Ltd., GB Patent 1016642 (1966).
2. Albright and Wilson Ltd., GB Patent 1017375 (1966).
3. V. Chandrasekhar and K.R.J. Thomas, *Struct. Bonding*, **81**, 41 (1993).
4. B. Zanin, J.P. Faucher and J.F. Labarre, *Inorg. Chim. Acta*, **172**, 147 (1990).
5. J.P. Bonnet and J.F. Labarre, *Inorg. Chim. Acta,* **149**, 187 (1988).
6. H. Ibisoglu, *Heterocycles*, **71**, 2173 (2007).
7. G. Yenilmez Ciftçi, E. Tanriverdi and Y. Zorlu, *Heterocycles*, **75**, 635 (2008).
8. R. Andrews, *IRCS Med. Sci*., **7**, 285 (1979).
9. G. Guerch, J.F. Labarre, R. Lahana, R. Roques and F. Sournies, *J. Mol. Struct*., **99**, 275 (1983).
10. J. Liebig, *Ann. Chem*., **11**, 139 (1834).
11. J.H. Gladstone and J.D. Holmes, *J. Chem. Soc*., **17**, 225 (1864).
12. C.W. Allen, *Chem. Rev*., **91**, 119 (1991).
13. R.N. Das, R.A. Shaw, B.C. Smith and M. Woods, *J. Chem. Soc., Dalton Trans*., 709 (1973).
14. D.J. Lingley, R.A. Shaw, M. Woods and S.S. Krishnamurthy, *Phosphorus Sulfur*, **4**, 379 (1978).
15. S. Das, R. Keat, R.A. Shaw and B.C. Smith, *J. Chem. Soc*., 5032 (1965).
16. N.V. Mani and A.J. Wagner, *Acta Crystallogr. B*, **27**, 51 (1971).
17. M.J. Begley, D.B. Sowerby and T.T. Bamgboye, *J. Chem. Soc., Dalton Trans*., 1401 (1979).
18. W. Polder and A.J. Wagner, *Cryst. Struct. Commun*., **5**, 253 (1976).
19. S. Ganapathiappan and S.S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.*, 585 (1987).
20. V.B. Desai, R.A. Shaw and B.C. Smith, *J. Chem. Soc. A*, 2023 (1970).
21. H. Lederle, G. Ottman and E. Kober, *Znorg. Chem.*, **5**, 1818 (1966).
22. D.D. Perrin and W.L.F. Armagedo, Purification of Laboratory Chemicals, Perjamon Press, Oxford, edn. 3 (1988).
23. S.A. Ahmed, R.A. Haque, Z.H. Zetty, H.-K. Fun and W.-S. Loh, *Acta Cryst.*, **E68**, o306 (2012).
24. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03, Revision C.02, Gaussian Inc., Wallingford CT (2004).
25. H. Koopman, F.J. Spruit, F. Van Deursen and J.Bakker, *Rec. Trav. Chem*., **84**, 341 (1965).
26. U. Kropacheva and V.A. Parshina, *Zhur. Obshchei. Khim.*, **35**, 1988 (1965).