

HEXACHLOROCYCLOTRIPHOSHAZENE: MACROMOLECULAR ASSEMBLIES IN VAPOR AND CRYSTALLINE PHASES. EXPERIMENTAL AND COMPUTATIONAL APPROACH

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Supplementary materials

S1. Synthesis of hexachlorocyclotriphosphazene (HCCP)

The well-known preparation procedure of HCCP¹ was modified by adding zinc powder in a stoichiometric amount and pyridine in a catalytic amount to the reaction mixture. Briefly, the mixture of 3.7485 g (0.018 mol) of phosphorus pentachloride PCl₅ in 20 ml of chlorobenzene was added dropwise to a suspension of 0.9624 g (0.018 mol) of ammonium chloride NH₄Cl and 1.2 g (0.02 mol) of zinc powder (14–50 mesh ASTM) in 30 ml of chlorobenzene. The reaction mixture was stirred under reflux until the indicator paper stopped indicating the acidic medium of hydrochloric acid releasing. As reaction had been proceeding, formation of precipitate was observed. The pale-yellow solid precipitate was treated with petroleum ether followed by the recrystallization from the hot petroleum ether as well. The desired white-crystalline product was obtained and then purified by solid-phase sublimation under $P = 10$ mmHg; $T = 373$ K and characterized by the ³¹P NMR spectroscopy (Figure 1), PXRD (Figure S2 in *Electronic Supplementary Materials*) and IR-spectroscopy (Figure S3). The corresponding data is presented here: **IR**: ν [cm⁻¹] = 1208, 873, 599, 520. **³¹P NMR** (191.96 MHz; CDCl₃): δ [ppm] = 20.03 (s, NPN) like in the literature data⁴⁹.

In the FTIR spectra of phosphazene, an interesting absorption peaks are displayed at 1212 and 1189 cm⁻¹ referring to the asymmetric and symmetric stretching vibration of P=N groups, respectively. The band at 874.8 cm⁻¹ assigned to P=N skeletal vibration. The characteristic absorption at 599.9, 519.8 cm⁻¹ are related to asymmetric and symmetric vibration of P–Cl bonds. Strong peak due to $\nu_a(\text{PNP})$ ring asymmetric stretching at 1212 cm⁻¹, together with a peak due to $\nu_s(\text{PNP})$ ring asymmetric stretching at 875 cm⁻¹ formed a weak combination band at 2085 cm⁻¹. Bands due to asymmetric and symmetric P–Cl stretching also appeared at 599.9 and 519.8 cm⁻¹, respectively.

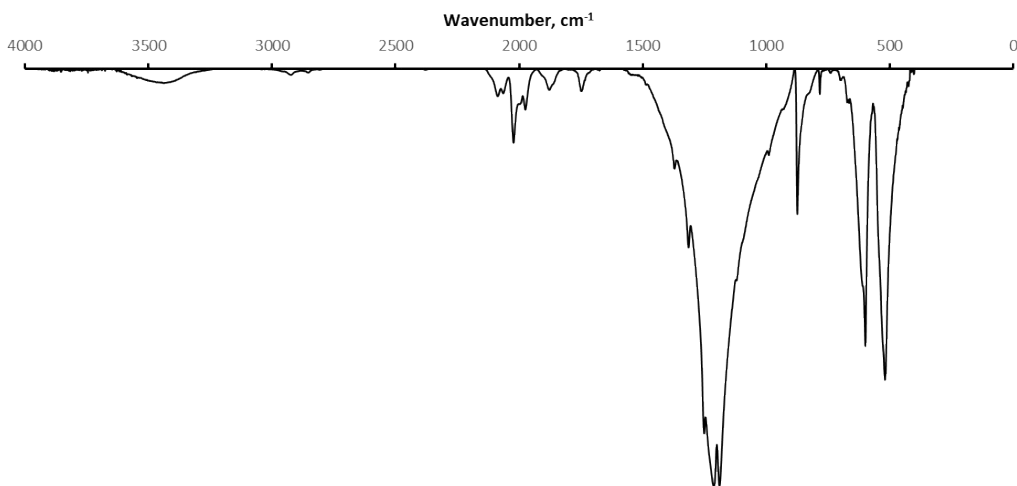


Figure S1.1. The IR-spectra of hexachlorocyclotriphosphazene

S2. Optimized geometries

All the coordinates are given in angstroms. The n_i value corresponds to the amount of imaginary frequencies detected.

$N_3P_3Cl_6$ by B3LYP-D3

$n_i = 0$

Cl	2.49936500	1.40741200	-1.57524600
Cl	2.49920600	1.40735900	1.57527600
Cl	-0.03056000	-2.86796300	1.57535400
Cl	-0.03070200	-2.86788500	-1.57532900
P	1.39524800	0.78580000	-0.00001400
P	-0.01715900	-1.60111900	0.00000100
N	1.35110500	-0.79943200	-0.00005200
N	-1.36812500	-0.77054200	0.00003900
Cl	-2.46855300	1.46064100	1.57527500
Cl	-2.46855200	1.46045200	-1.57528200
P	-1.37820200	0.81537300	-0.00000600
N	0.01676900	1.56982000	-0.00006200

$N_3P_3Cl_6$ by APFD

$n_i = 0$

Cl	-2.26820200	1.72326700	-1.56166200
Cl	-2.26812700	1.72319300	1.56170400

Cl	2.62643400	1.10265800	1.56171200
Cl	2.62649900	1.10261100	-1.56167800
P	-1.26748600	0.96299600	-0.00001700
P	1.46773400	0.61618700	-0.00000600
N	0.19751000	1.55762700	-0.00004700
N	1.25021900	-0.94987000	0.00002200
Cl	-0.35834600	-2.82585600	1.56169400
Cl	-0.35826800	-2.82588500	-1.56170200
P	-0.20024700	-1.57916800	-0.00001700
N	-1.44770800	-0.60775800	-0.00005700

(N₃P₃Cl₆)₄ by B3LYP-D3

$n_i = 0$

Cl	0.21617000	2.22959700	2.40337200
Cl	1.87421300	-0.05594600	1.03328100
Cl	5.15212200	3.64496100	-0.44238900
Cl	3.28820600	5.64331100	1.12212600
P	1.47248400	1.90060300	0.84387700
P	3.22900600	3.90538600	0.08038700
N	2.79747000	2.73991300	1.06586000
N	2.36047800	4.12803100	-1.23143600
Cl	1.01865500	2.63349700	-3.38211000
Cl	-0.54220700	4.61968000	-1.51176900
P	1.01708800	3.32638400	-1.48245900
N	0.67635200	2.12345400	-0.51049300
Cl	2.75094700	-3.49445400	1.05303900
Cl	5.65002000	-4.37506900	0.19306400
Cl	7.73361100	-0.52625000	1.90881800
Cl	5.04887100	0.81934400	2.85162300
P	4.51340900	-2.71753600	0.47893300
P	5.75776400	-0.44145600	1.45682900
N	5.11822800	-1.87647500	1.68001100
N	5.59495700	0.22564700	0.02589900
Cl	6.42888000	-0.80019600	-2.61308600
Cl	3.65846000	0.60493200	-2.15031800
P	4.98947600	-0.57417300	-1.19992600
N	4.31606200	-1.98194900	-0.91533800

Cl	-3.79076700	-4.93957600	-1.49842700
Cl	-4.66690600	-1.92420400	-1.63157600
Cl	0.30614200	-0.84204800	-2.46110000
Cl	0.82091600	-3.93795600	-2.28131400
P	-3.08943000	-3.07515200	-1.12151000
P	-0.41732100	-2.49998400	-1.57774400
N	-1.88809600	-2.76822900	-2.11022400
N	-0.21505500	-2.37125200	-0.01124200
Cl	-1.46228800	-1.19233500	2.37196400
Cl	-0.83564900	-4.26742600	2.15429200
P	-1.38029400	-2.67234300	1.01854800
N	-2.83174900	-2.93176800	0.43600300
Cl	-7.24905300	0.46258700	-2.25880300
Cl	-7.75309500	2.94775600	-0.39557200
Cl	-3.19495100	3.23760300	0.95945100
Cl	-2.31229300	0.77435400	-0.77148400
P	-6.55533800	1.32152200	-0.56707400
P	-3.90678200	1.48731800	0.22347600
N	-5.06520300	1.80283000	-0.81482400
N	-4.23801600	0.52056900	1.43476400
Cl	-6.30233600	0.74374000	3.52627300
Cl	-5.67936700	-1.96609500	2.05165100
P	-5.71280700	0.01586500	1.72583400
N	-6.83256500	0.34305700	0.64892600

(N₃P₃Cl₆)₄ by APFD

$n_i = 0$

Cl	0.41331800	2.19541600	2.49781800
Cl	1.91196500	-0.11999000	1.05497400
Cl	5.17177200	3.61973100	-0.52914800
Cl	3.33495200	5.51982500	1.13100300
P	1.56038100	1.83009700	0.88507400
P	3.28023400	3.81798300	0.06133600
N	2.91801300	2.62427900	1.03375500
N	2.36824500	4.05299600	-1.21332700
Cl	0.89354500	2.60332000	-3.27549400
Cl	-0.52011300	4.57804000	-1.32270800

P	1.00468000	3.27382700	-1.38983900
N	0.69451200	2.06862300	-0.41744300
Cl	2.72412700	-3.51588000	0.98744300
Cl	5.58394700	-4.33770900	0.03782600
Cl	7.68282100	-0.58576800	1.76878500
Cl	5.07068700	0.72054500	2.86691300
P	4.45179000	-2.71481200	0.39908700
P	5.70675900	-0.47786000	1.40900300
N	5.07447900	-1.91434400	1.61304600
N	5.48798600	0.24507800	0.01815200
Cl	6.32546700	-0.74438200	-2.61301200
Cl	3.58006000	0.64919300	-2.14671800
P	4.89052800	-0.53830400	-1.21662800
N	4.21221400	-1.94563000	-0.96555200
Cl	-3.85258300	-4.79582200	-1.39769300
Cl	-4.66808100	-1.79987200	-1.65043100
Cl	0.34863000	-0.88793500	-2.40311900
Cl	0.71256500	-3.97791200	-2.20588800
P	-3.13080800	-2.94545900	-1.08204700
P	-0.44972800	-2.49219800	-1.52350000
N	-1.92126100	-2.69472700	-2.06991400
N	-0.24488900	-2.36119900	0.03825900
Cl	-1.42024600	-1.14019000	2.41023800
Cl	-1.00238200	-4.21991700	2.16345000
P	-1.43374300	-2.59518700	1.05261100
N	-2.89471600	-2.75048200	0.46879800
Cl	-7.09763100	0.69712300	-2.36341800
Cl	-7.54597600	3.07932000	-0.39766900
Cl	-3.07388400	3.06000400	1.12969700
Cl	-2.23098000	0.72088000	-0.73904200
P	-6.42941900	1.42455600	-0.62090600
P	-3.81679500	1.41205600	0.24939900
N	-4.91757100	1.85082100	-0.80044800
N	-4.21899900	0.37456100	1.37171400
Cl	-6.30742800	0.71441500	3.39742300
Cl	-5.85062800	-1.98696700	1.90635800
P	-5.73027600	-0.02133300	1.61468500

N	-6.79811600	0.39667200	0.52251600
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(N₃P₃Cl₆)₈ by B3LYP-D3

$n_i = 0$

Cl	2.14776600	-2.72818900	0.92080500
Cl	-0.88430400	-1.93926800	0.70602800
Cl	0.86718500	1.14215400	-3.24277600
Cl	3.61462100	-0.26366800	-2.61007700
P	0.95011000	-1.18930200	0.37966300
P	1.91552900	0.34174400	-1.71027800
N	1.12462100	-0.92692100	-1.17810800
N	2.26981700	1.48333400	-0.66711300
Cl	0.22136900	2.79178600	1.01469700
Cl	3.11488800	2.15526100	2.05738500
P	1.70897600	1.43384800	0.82152800
N	1.20548800	0.02856100	1.36344000
Cl	-3.61499700	-4.11611800	1.04828600
Cl	-6.50961800	-3.58736700	-0.02590600
Cl	-4.84687200	-1.08632300	-3.84075100
Cl	-1.88465300	-1.26248700	-2.82041100
P	-4.67006200	-2.73459500	0.03252800
P	-3.77676100	-1.24907700	-2.12842000
N	-4.09833900	-2.64415500	-1.44580500
N	-3.99692400	0.06436900	-1.27021800
Cl	-5.97737200	1.25490200	0.53766000
Cl	-2.97491600	0.91247400	1.36749800
P	-4.41095900	0.02215400	0.26117100
N	-4.73439100	-1.40077200	0.88708900
Cl	1.01226300	-9.59865200	-0.47456600
Cl	3.50527500	-7.69191900	-0.33198900
Cl	0.41592900	-5.02051900	3.10395800
Cl	-1.68772900	-7.21420000	2.30587700
P	1.49654500	-7.65091200	-0.18441100
P	-0.08171300	-6.20964100	1.56112500
N	1.10034000	-7.23514300	1.29739900
N	-0.56204200	-5.30959100	0.35043800
Cl	0.34515300	-4.01014800	-2.11793400

Cl	-1.89762800	-6.21407500	-2.11658600
P	-0.19978100	-5.68085900	-1.14996900
N	0.90876100	-6.79365000	-1.38142700
Cl	-9.71068900	-5.14355100	0.10182300
Cl	-12.33907000	-3.49140200	0.61663700
Cl	-10.65875800	0.46357400	-1.35275300
Cl	-7.83955500	-0.77215900	-1.99194700
P	-10.33093300	-3.25751600	0.46342100
P	-9.35355100	-0.92808700	-0.66779700
N	-10.01022800	-2.36569800	-0.80885700
N	-8.83903000	-0.48379300	0.76278300
Cl	-10.22130300	-0.28619900	3.35537700
Cl	-7.36220900	-1.57075000	3.05935100
P	-9.09232700	-1.36212800	2.05932500
N	-9.75469600	-2.79168100	1.86474200
Cl	-2.37194100	2.68241000	-1.90645000
Cl	-0.07695600	4.83005000	-2.12290900
Cl	-2.32661100	6.84032900	2.19289700
Cl	-4.29999400	4.40529900	1.90445800
P	-1.97100500	4.61650800	-1.48764500
P	-3.15386200	5.65798000	0.79504100
N	-2.00668100	4.81934100	0.08913700
N	-4.10261900	6.53370500	-0.12768700
Cl	-3.91544800	8.30447700	-2.46791000
Cl	-5.85472200	5.82203500	-2.39033100
P	-4.04856600	6.43561500	-1.70907600
N	-2.91576800	5.54336700	-2.36518800
Cl	7.02742400	-8.30006600	-0.57777600
Cl	9.15498700	-6.00810300	-0.20589300
Cl	6.46416700	-3.58162700	2.87146700
Cl	4.01893900	-5.54242100	2.60120900
P	7.15163600	-6.32270500	-0.19890800
P	5.59729000	-4.84918700	1.55480500
N	6.59186800	-6.04976800	1.26003600
N	5.05911500	-4.01521200	0.31944000
Cl	6.36600700	-2.63543200	-1.93594900
Cl	3.88399800	-4.53091200	-2.31891700

P	5.52058500	-4.30545200	-1.17010700
N	6.49707400	-5.53430200	-1.40851100
Cl	8.11498400	-0.81409000	0.85182600
Cl	4.97602100	-0.68952500	0.90236000
Cl	5.57577900	2.80572900	-2.98862000
Cl	8.64215100	2.24250300	-2.58554000
P	6.56966400	0.45584500	0.49173900
P	6.89162400	2.28839900	-1.55623200
N	6.55974100	0.81999900	-1.05412900
N	6.95463400	3.44839400	-0.47686200
Cl	5.83616700	4.42523300	2.05221600
Cl	8.86053300	3.58613800	1.77832100
P	7.00997800	3.12330700	1.07665800
N	6.63705600	1.64994600	1.53454400
Cl	3.23892300	4.54322100	-0.89236300
Cl	5.05529300	7.07215800	-0.42420400
Cl	2.84299200	7.94486800	3.86795700
Cl	0.90330500	5.50517600	3.43611400
P	3.20728300	6.35039500	-0.02045300
P	1.94481000	6.88210300	2.39473900
N	3.06790700	6.15082500	1.54931400
N	0.92521500	7.82357500	1.62498500
Cl	1.70311900	10.11400700	-0.07302900
Cl	-0.66079400	8.19045500	-0.82644000
P	1.13029500	8.16997000	0.08981000
N	2.12554700	7.26064900	-0.74527800

$N_3P_3Cl_5^+$ by B3LYP-D3

$n_i = 0$

Cl	-2.48470900	-1.13143200	-1.58533200
Cl	-2.47685900	-1.13361800	1.58709900
Cl	0.00000500	3.67814500	0.00146700
P	-1.42302100	-0.59172100	-0.00150500
P	0.00002100	1.74727900	0.00038600
N	-1.38827200	1.06542600	-0.00008200
N	1.38830000	1.06543000	-0.00015100
Cl	2.47683600	-1.13357200	1.58711100

Cl	2.48472000	-1.13150500	-1.58530200
P	1.42300100	-0.59174200	-0.00151200
N	-0.00001000	-1.26993500	-0.00637500

[N₃P₃Cl₅·N₃P₃Cl₆]⁺ by B3LYP-D3

$n_i = 0$

Cl	2.93041100	-2.98985900	0.47001800
Cl	4.66462500	-1.28927700	2.49361000
Cl	0.65105100	2.23151900	1.44382700
Cl	-0.00048900	0.00192600	-0.84798200
P	3.49868500	-1.11003200	0.88749300
P	1.70750800	0.91325300	0.44330600
N	2.18185300	-0.27714200	1.33714800
N	2.59275000	1.55289500	-0.67126800
Cl	5.42064500	2.07608900	-1.17597500
Cl	3.66676200	0.26845000	-3.09012200
P	3.92146200	0.76440800	-1.16783800
N	4.31293000	-0.51749700	-0.32836600
Cl	-0.65028100	-2.23461500	1.43926900
Cl	-2.92620000	2.98704200	0.47158800
Cl	-4.66413100	1.29052300	2.49551700
P	-1.70879400	-0.91512200	0.44309200
P	-3.49855800	1.10859600	0.88964000
N	-2.18342800	0.27292600	1.33973200
N	-4.31393900	0.51699500	-0.32590100
Cl	-3.66822200	-0.26349700	-3.08955200
Cl	-5.42118100	-2.07501600	-1.17819500
P	-3.92233100	-0.76300200	-1.16820800
N	-2.59308400	-1.55208600	-0.67367700

S3. Supporting Tables and Figures

Table S3.1. Positions of atoms in the HCCP lattice structure

N	Label	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	Cl1	Cl	0.31235(4)	0.25	0.45314(10)	x,y,z
2	Cl2	Cl	0.39792(4)	0.25	0.92081(10)	x,y,z
3	Cl3	Cl	0.68246(3)	0.45138(4)	0.60815(7)	x,y,z

4	Cl4	Cl	0.58520(3)	0.42968(4)	0.15248(7)	x,y,z
5	P1	P.3	0.43926(4)	0.25	0.60760(10)	x,y,z
6	P2	P.3	0.59529(3)	0.35721(4)	0.44158(7)	x,y,z
7	N1	N.2	0.49286(10)	0.35596(12)	0.5560(2)	x,y,z
8	N2	N.2	0.64903(14)	0.25	0.4058(3)	x,y,z
9	Cl3	Cl	0.68246(3)	0.04862(4)	0.60815(7)	x,1/2-y,z
10	Cl4	Cl	0.58520(3)	0.07032(4)	0.15248(7)	x,1/2-y,z
11	P2	P.3	0.59529(3)	0.14279(4)	0.44158(7)	x,1/2-y,z
12	N1	N.2	0.49286(10)	0.14404(12)	0.5560(2)	x,1/2-y,z

Table S3.2. Bond length values in the HCCP lattice structure

Number	Atom1	Atom2	Polymeric	Cyclicity	Length, Å
1	Cl1	P1	no	acyclic	1.9941(5)
2	Cl2	P1	no	acyclic	1.9896(5)
3	Cl3	P2	no	acyclic	1.9859(6)
4	Cl4	P2	no	acyclic	1.9939(6)
5	P1	N1	no	cyclic	1.580(1)
6	P1	N1	no	cyclic	1.580(1)
7	P2	N1	no	cyclic	1.581(1)
8	P2	N2	no	cyclic	1.578(1)
9	N2	P2	no	cyclic	1.578(1)
10	Cl3	P2	no	acyclic	1.9859(6)
11	Cl4	P2	no	acyclic	1.9939(6)
12	P2	N1	no	cyclic	1.581(1)

Table S3.3. Bond angles values in the HCCP lattice structure

Number	Atom1	Atom2	Atom3	Angle
1	Cl1	P1	Cl2	101.37(4)
2	Cl1	P1	N1	108.73(3)
3	Cl1	P1	N1	108.73(3)

4	Cl2	P1	N1	109.01(3)
5	Cl2	P1	N1	109.01(3)
6	N1	P1	N1	118.61(3)
7	Cl3	P2	Cl4	102.09(3)
8	Cl3	P2	N1	109.13(6)
9	Cl3	P2	N2	108.22(3)
10	Cl4	P2	N1	109.27(6)
11	Cl4	P2	N2	108.50(2)
12	N1	P2	N2	118.39(3)
13	P1	N1	P2	121.22(3)
14	P2	N2	P2	121.10(2)
15	N2	P2	Cl3	108.22(3)
16	N2	P2	Cl4	108.51(3)
17	N2	P2	N1	118.39(4)
18	Cl3	P2	Cl4	102.09(3)
19	Cl3	P2	N1	109.13(6)
20	Cl4	P2	N1	109.27(6)
21	P1	N1	P2	121.22(3)

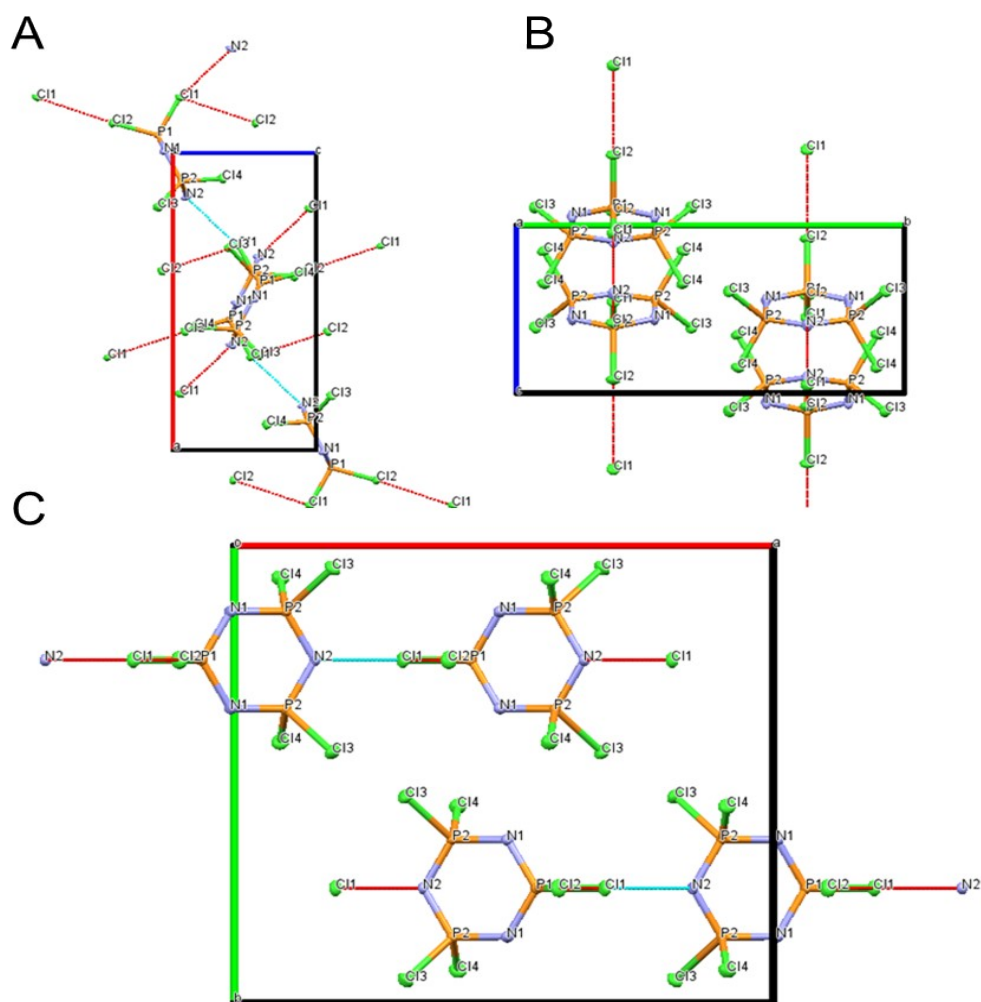


Figure S3.1. The crystalline structure of HCCP obtained by the X-ray Diffraction Analysis. The simplest intermolecular assembly is represented. A: through a-axis; B: through b-axis; C: through c-axis.

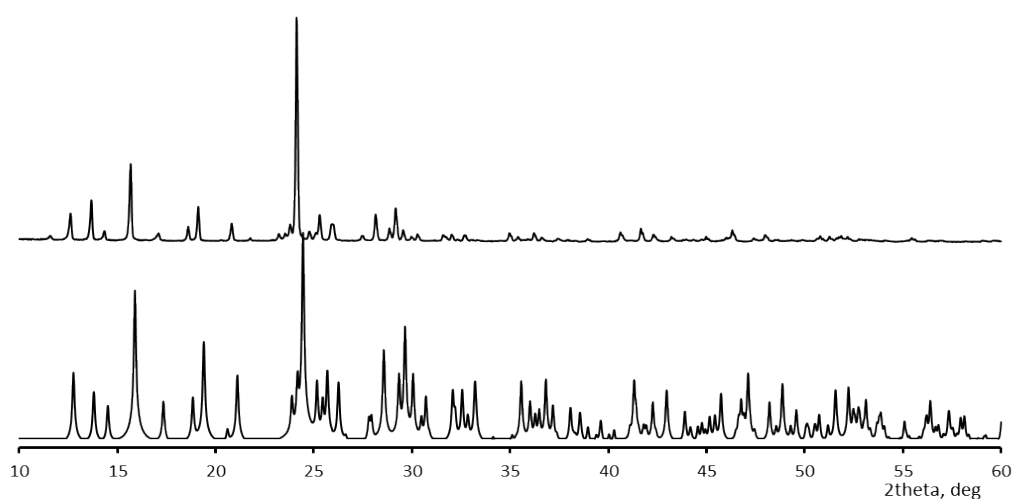


Figure S3.2. Up: the experimental pattern; down: the simulated from the cif-file