Molecular Insights into the Effect of Small Molecule Impurities in the Ring-Opening Polymerization of $[PCl_2N]_3$ using Quantum Mechanical Analysis

Supplemental Information

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Table S1. The activation energy (E_a, in kJ/mol) for the hydrolysis and tautomerization catalyzed by HCl, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q and the CCSD(T)/aTZ level of theory.

Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
R	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS[c]	186.84	187.42	166.96	186.11	201.28	182.70	193.57	185.76	154.40	173.20	177.33	180.99
P_1HB[c]	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS_HB	1.04	1.26	1.18	1.13	0.03	1.77	0.96	0.57	0.01	N/A	N/A	N/A
P_2HB	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
SPT_TS[c]	14.79	15.92	13.73	11.40	17.93	15.09	15.73	10.44	16.91	16.47	16.14	20.09
P	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a]Functional or method. [b]Not found using the computational software [c]Stationary points have different electronic structures at the M06-2X/6-311+G(d,p) level of theory when compared to the structures characterized at the other levels of theory. [d]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory

Table S2. The activation energy (E_a, in kJ/mol) for the tautomerization reaction without interference, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q and the CCSD(T)/aTZ level of theory.

Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
Tauto_R	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tauto_TS	143.76	143.03	142.55	136.92	146.56	148.76	147.49	138.19	139.91	139.01	139.84	146.24
Tauto_P	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a]Functional or method [b]Compound and basis set [c]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory

Table S3. The activation energy (E_a, in kJ/mol) for the ring-opening reaction initiated by HCl, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q and the CCSD(T)/aTZ level of theory.

Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
R'	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS1'	116.13	115.84	109.04	113.13	124.00	113.06	121.45	111.75	111.00	116.48	117.33	118.82
Int'	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS2'	10.41	7.53	8.51	7.25	8.55	8.94	8.99	7.87	13.08	13.43	14.50	12.23
P'	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a]Functional or method [b]Compound and basis set [c]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory

Table S4. The percent of energy deviation (%) of hydrolysis and tautomerization catalyzed by HCl, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q compared with the results obtained at the CCSD(T)/aTZ||MP2/aTZ level of theory.

Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
R	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS[c]	3.2	3.6	-7.8	2.8	11.2	0.9	7.0	2.6	-14.7	-4.3	-2.0	N/A
P_1HB[c]	-3.3	-10.8	-16.4	-20.9	-15.7	16.0	8.1	-22.2	-32.8	-15.4	-15.1	N/A
TS_HB	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
P_2HB	-8.7	-12.6	-9.8	-15.7	-8.0	-1.6	3.5	-11.1	-28.9	-6.8	-6.6	N/A
SPT_TS[c]	2.0	-7.6	3.4	0.9	-6.3	12.5	18.7	11.1	-36.7	-0.1	1.3	N/A
P	0.3	9.9	11.0	0.4	8.0	3.8	21.9	1.5	-27.6	-7.7	-7.7	N/A

[a]Functional or method. [b]Not found using the computational software [c]Stationary points have different electronic structures at the M06-2X/6-311+G(d,p) level of theory when compared to the structures characterized at the other levels of theory. [d]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory

Table S5. The percent of energy deviation (%) of the tautomerization reaction without interference, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q compared with the results obtained at the CCSD(T)/aTZ||MP2/aTZ level of theory.

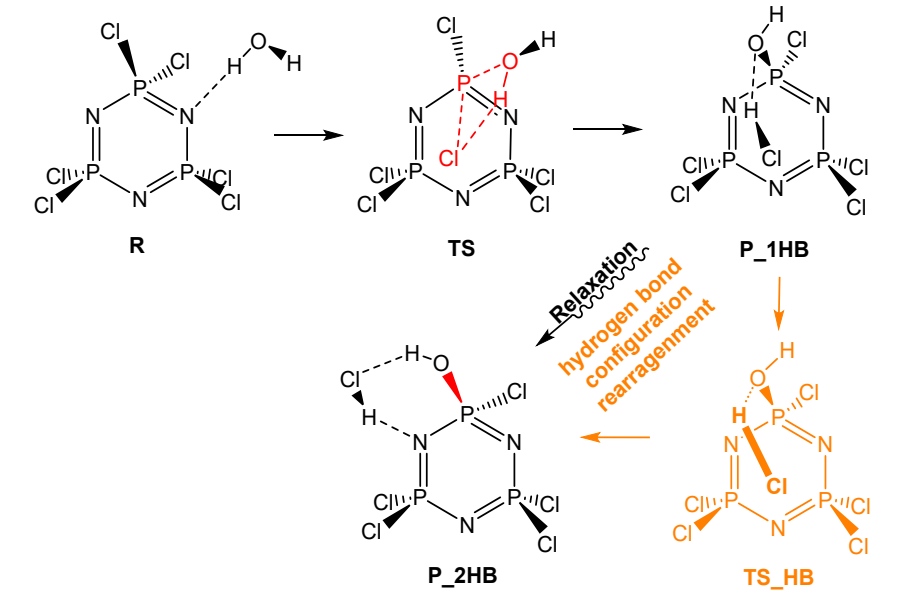
Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
Tauto_R	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tauto_TS	-1.7	-2.2	-2.5	-6.4	0.2	1.7	0.9	-5.5	-4.3	-4.9	-4.4	N/A
Tauto_P	-33.5	-186.8	-233.5	-153.7	-166.0	-105.2	-146.9	-132.8	15.1	-4.5	6.2	N/A

[a]Functional or method [b]Compound and basis set [c]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory

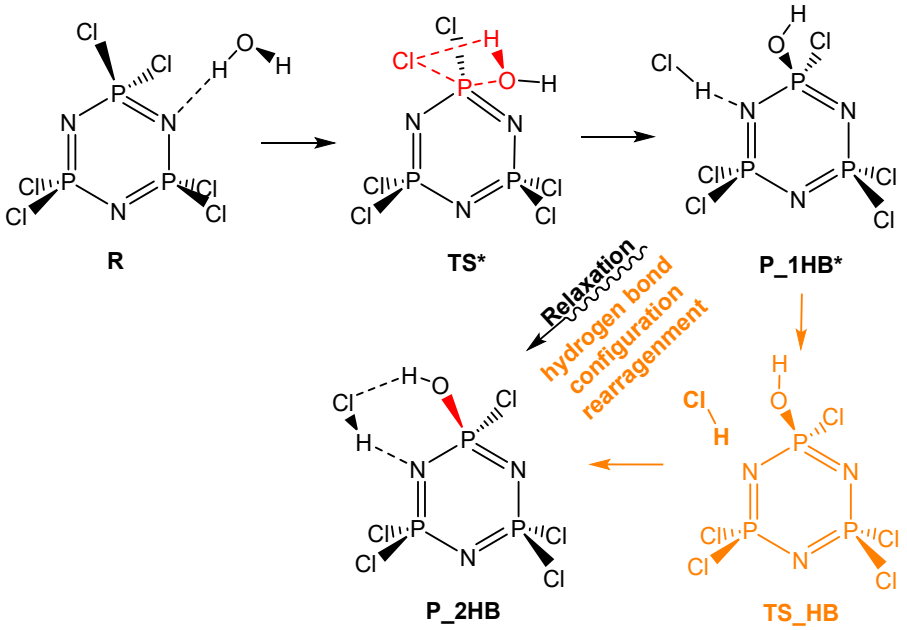
Table S6. The percent of energy deviation (%) of the ring-opening reaction initiated by HCl, determined at different DFT levels of theory, the MP2/aXZ levels of theory where X = D, T and Q compared with the results obtained at the CCSD(T)/aTZ||MP2/aTZ level of theory.

Theory	**DFT**								***ab initio***			
F/M[a]	B3LYP		B3LYP-D3	B3PW91	ωB97X-D	M06-2X	cam-B3LYP	PBE0	MP2			CCSD(T)
C/B[b]	aTZ	6-311+G(d,p)							aDZ	aTZ	aQZ[c]	aTZ[c]
R'	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
TS1'	-2.3	-2.5	-8.2	-4.8	4.4	-4.8	2.2	-6.0	-6.6	-2.0	-1.3	N/A
Int'	5.0	4.0	-3.9	-1.1	7.8	-6.8	8.0	-3.9	-13.3	-6.3	-4.5	N/A
TS2'	3.0	-0.3	-6.5	-5.1	4.0	-8.8	4.5	-7.1	-11.3	-4.7	-2.2	N/A
P'	7.2	3.5	-6.6	-3.3	5.4	-14.3	6.7	-7.1	-17.1	-6.4	-3.4	N/A

[a]Functional or method [b]Compound and basis set [c]Single-point energies completed based on the electronic structures fully optimized at the MP2/aTZ level of theory



(a).



(b).

Scheme S1. The stationary point for the hydrolysis reaction characterized at (a). the B3LYP/6-311+G(d,p) level of theory* and the (b). M06-2X/6-311+G(d,p) level of theory.

*The stationary points are consistent with the electronic structure characterized at the MP2/aTZ level of theory. The transition state associated with the hydrogen bond configuration rearrangement (TS_HB, colored in orange) can be identified using the DFT method and at lower levels of theory for MP2 calculations, it could not be found at MP2/aTZ level of theory.

Section 2. Harmonic vibrational frequencies (ω in cm−1) and infrared intensities (IR in km mol−1) for the pivotal energy minima in the reaction mechanisms

Table S7. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the reactants (**R**) for the hydrolysis reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	MP2/aTZ		B3LYP/6-311+G(d,p)	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	9	1.1	15	1.3
2	15	5.2	29	3.0
3	17	0.2	33	0.0
4	24	0.2	34	0.2
5	29	1.2	42	1.4
6	96	75.9	104	88.8
7	117	0.0	112	0.1
8	122	0.4	116	3.0
9	155	0.0	150	0.0
10	155	0.0	150	0.0
11	171	0.0	168	0.0
12	200	3.0	192	0.1
13	200	0.0	192	1.9
14	215	3.8	210	5.5
15	220	4.7	215	5.3
16	277	88.7	281	76.8
17	318	0.0	308	0.0
18	321	0.0	313	0.0
19	329	9.5	322	4.3
20	330	14.5	328	24.4
21	339	14.7	332	6.9
22	365	0.0	344	0.0
23	391	3.8	380	1.9
24	518	18.7	502	238.7
25	545	310.8	512	335.6
26	552	288.6	552	16.7
27	588	1.7	553	1.2
28	592	8.9	566	104.0
29	621	526.9	605	581.0
30	655	3.5	655	1.4
31	788	3.1	762	4.4
32	877	8.9	843	18.9
33	884	0.6	852	3.6
34	1170	32.2	1115	45.5
35	1231	1046.6	1204	1181.2
36	1244	1151.9	1227	1293.8
37	1638	28.8	1630	33.7
38	3713	333.9	3727	332.1
39	3905	155.1	3889	118.5

Table S8. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the product with 1 hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	31	0.3	10	0.6
2	35	1.3	16	0.5
3	40	0.9	35	0.1
4	41	0.2	40	0.1
5	49	0.8	42	0.3
6	76	0.5	77	1.7
7	117	19.0	122	1.1
8	132	9.7	154	1.4
9	159	0.2	170	11.1
10	177	4.3	173	4.0
11	188	0.4	188	5.9
12	199	6.5	202	2.4
13	211	7.0	214	4.8
14	223	5.8	245	1.3
15	259	4.7	280	14.1
16	291	44.2	315	8.3
17	313	40.9	321	4.3
18	330	7.9	326	2.1
19	336	4.3	329	6.6
20	343	4.9	333	2.4
21	353	19.5	362	22.4
22	388	25.8	384	33.9
23	401	19.1	390	15.0
24	419	13.6	409	28.4
25	540	272.9	510	340.1
26	556	234.0	531	258.9
27	586	24.3	551	2.6
28	611	482.5	591	464.1
29	646	4.7	641	44.4
30	768	75.1	743	83.0
31	867	46.5	835	65.6
32	882	12.5	855	18.4
33	947	109.4	917	157.5
34	1059	100.8	1046	126.4
35	1177	2.3	1130	4.3
36	1237	1030.1	1217	1248.1
37	1245	926.5	1230	1123.7
38	2982	111.0	2853	355.8
39	3785	165.7	3797	167.8

Table S9. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the product with 2 hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	17	0.0	21	0.1
2	22	0.0	35	0.1
3	29	0.2	39	0.2
4	32	0.2	42	0.7
5	74	5.3	63	3.9
6	113	5.3	101	5.6
7	129	0.5	122	1.0
8	159	0.1	155	0.1
9	185	1.8	175	2.5
10	185	0.1	180	0.3
11	206	0.7	198	1.2
12	215	2.6	206	2.9
13	256	0.7	242	1.1
14	264	0.3	256	0.9
15	330	6.8	321	3.1
16	337	3.9	327	1.5
17	345	1.8	334	0.8
18	348	16.6	335	11.5
19	363	6.1	347	11.6
20	402	7.9	381	6.8
21	412	26.8	394	32.3
22	444	39.7	417	65.8
23	539	58.6	512	331.1
24	546	292.5	520	126.4
25	564	133.5	542	65.6
26	589	9.9	562	35.7
27	614	462.1	597	453.1
28	640	89.9	627	192.2
29	689	139.3	667	69.9
30	770	85.0	744	89.6
31	868	61.0	837	73.0
32	881	7.2	848	10.1
33	988	108.1	947	154.7
34	1117	106.9	1056	103.7
35	1164	95.2	1115	82.2
36	1226	900.9	1201	1023.0
37	1258	1124.3	1243	1274.2
38	2514	1420.0	2499	1184.1
39	3598	538.8	3651	431.4

Table S10. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the products (**P**) for the hydrolysis reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	19	0.0	20	0.1
2	26	0.0	37	0.5
3	34	0.3	38	0.3
4	50	0.0	44	0.1
5	77	6.2	53	4.8
6	114	2.6	105	3.0
7	127	3.0	121	2.5
8	161	0.5	155	1.1
9	177	0.8	173	0.3
10	188	4.9	181	6.1
11	199	2.0	192	2.9
12	219	2.5	211	0.6
13	263	41.3	249	30.5
14	280	1.5	273	3.5
15	311	5.8	304	2.0
16	333	6.7	324	7.2
17	343	2.9	331	1.3
18	353	0.6	336	0.9
19	376	22.1	358	17.7
20	411	2.3	391	1.8
21	428	27.1	412	32.2
22	512	44.6	500	79.4
23	538	103.0	507	62.2
24	550	241.0	513	277.8
25	596	4.3	552	11.3
26	604	6.1	572	10.9
27	619	470.1	596	538.7
28	637	78.4	611	239.5
29	706	223.3	640	54.0
30	754	74.4	715	122.2
31	830	33.0	792	49.9
32	876	61.2	839	71.4
33	990	182.2	941	190.3
34	1208	121.3	1206	207.4
35	1239	203.9	1227	393.0
36	1282	904.7	1288	1117.8
37	1320	750.7	1335	467.1
38	2425	1257.1	2514	940.8
39	3390	620.5	3451	378.7

Table S11. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	4	0.3	8	0.3
2	16	0.1	28	0.6
3	18	0.5	33	0.0
4	24	0.0	33	0.2
5	26	0.0	42	0.2
6	95	2.6	85	2.4
7	122	0.0	115	0.0
8	155	0.0	150	0.0
9	155	0.0	150	0.0
10	171	0.0	168	0.0
11	199	0.2	191	0.0
12	200	0.0	192	0.1
13	215	3.0	210	4.1
14	222	0.7	215	1.3
15	318	0.1	309	0.0
16	318	0.2	311	0.4
17	321	0.0	313	0.0
18	328	9.7	321	4.7
19	341	18.8	333	8.4
20	366	0.0	344	0.0
21	387	3.5	376	0.2
22	474	1.5	486	0.1
23	537	157.8	505	263.8
24	547	326.7	513	357.5
25	558	115.6	555	43.6
26	590	2.3	556	0.0
27	592	0.9	556	4.7
28	623	526.2	609	583.9
29	657	2.4	657	1.2
30	785	15.2	758	18.0
31	873	26.6	839	38.5
32	885	1.2	853	5.0
33	1168	51.8	1111	75.1
34	1229	986.3	1201	1112.5
35	1246	1214.2	1229	1353.4
36	2717	1136.9	2666	917.3

Table S12. Harmonic vibrational frequencies (ω in cm−1) and infrared intensities (IR intensity in km mol−1) for the intermediate (Int') for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	27	0.1	2	0.1
2	35	0.0	31	0.1
3	56	0.2	32	0.0
4	85	0.8	76	1.9
5	102	1.0	93	10.3
6	134	6.8	111	19.3
7	146	0.5	146	1.8
8	158	0.3	152	0.5
9	178	0.5	169	1.6
10	205	1.7	191	0.8
11	212	1.1	198	18.9
12	250	3.9	210	59.1
13	258	27.4	230	0.2
14	274	8.9	250	9.0
15	286	48.4	279	14.8
16	317	6.3	279	1.7
17	326	8.9	315	0.2
18	346	2.9	325	0.0
19	369	14.9	331	1.1
20	380	2.5	349	10.5
21	422	8.9	377	0.4
22	499	215.7	463	268.2
23	534	264.8	507	314.2
24	548	13.8	528	7.1
25	580	14.4	548	8.6
26	584	66.6	583	375.2
27	619	437.2	643	213.3
28	654	18.0	646	24.9
29	731	41.7	707	33.6
30	789	101.2	756	97.4
31	861	41.3	812	27.1
32	957	240.9	903	283.7
33	1180	484.1	1220	617.5
34	1252	1000.4	1302	868.7
35	1265	188.2	1315	644.2
36	3513	115.3	3448	162.9

Table S13. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the product (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	17	0.2	22	0.6
2	28	0.0	29	0.0
3	54	0.3	35	0.4
4	93	0.1	90	2.3
5	97	0.2	92	0.5
6	127	3.0	107	17.3
7	154	1.4	145	2.0
8	157	0.2	151	0.1
9	174	2.0	164	2.8
10	194	0.2	189	0.6
11	217	2.4	204	3.7
12	256	6.3	231	19.0
13	259	0.6	245	0.4
14	273	6.8	255	9.3
15	303	6.5	289	4.2
16	316	12.7	298	3.3
17	332	4.0	313	1.9
18	353	1.4	327	4.8
19	367	4.6	345	2.0
20	389	27.5	357	45.6
21	403	4.6	372	1.4
22	468	368.1	411	443.2
23	492	50.6	481	5.2
24	538	176.0	490	93.2
25	561	52.7	518	243.6
26	576	86.3	532	59.1
27	584	179.3	554	77.5
28	622	404.7	588	541.0
29	660	19.7	648	14.2
30	789	14.9	766	11.6
31	874	10.3	840	6.2
32	1007	175.7	994	184.7
33	1205	298.3	1211	579.1
34	1227	420.9	1257	279.6
35	1278	1043.8	1289	1206.5
36	3547	56.8	3566	57.9

Table S14. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the reactant of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

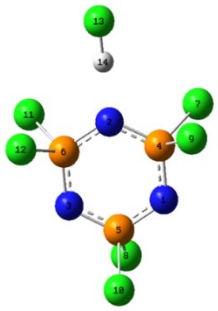
Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	22	0.0	35	0.0
2	30	0.1	39	0.3
3	32	0.1	39	0.0
4	124	5.0	120	2.6
5	157	11.4	153	3.0
6	164	20.0	165	24.6
7	179	1.0	171	1.2
8	190	5.7	186	7.7
9	205	2.8	199	2.3
10	221	6.5	214	7.4
11	252	5.4	244	5.7
12	286	26.7	282	37.2
13	329	7.1	320	3.1
14	338	4.3	325	4.3
15	342	1.1	331	1.6
16	346	11.1	333	3.4
17	363	8.4	358	12.5
18	400	12.5	377	9.5
19	414	20.5	404	36.6
20	542	302.2	507	338.0
21	551	227.6	526	251.0
22	583	6.9	546	1.8
23	609	452.8	588	477.4
24	644	16.9	640	36.7
25	769	61.1	743	61.7
26	869	51.9	837	61.0
27	880	16.2	847	24.4
28	966	154.3	929	186.7
29	1051	69.8	1015	60.5
30	1176	8.2	1130	7.4
31	1234	1105.8	1214	1241.4
32	1251	970.2	1234	1121.7
33	3799	173.2	3808	165.0

Table S15. Harmonic vibrational frequencies (ω in cm^{-1}) and infrared intensities (IR intensity in km mol^{-1}) for the product of the tautomerization reaction without the interferences of HCl (**Tauto_P**) fully optimized at the MP2/aTZ and the B3LYP/6-311+G(d,p) level of theory.

Level of theory	**MP2/aTZ**		**B3LYP/6-311+G(d,p)**	
Term/Vibration #	**ω**	**IR intensity**	**ω**	**IR intensity**
1	27	0.0	37	0.0
2	39	0.5	39	0.5
3	53	0.1	45	0.7
4	120	0.2	114	0.1
5	160	0.0	154	0.3
6	173	0.8	170	0.2
7	181	0.2	174	0.5
8	195	1.9	190	2.6
9	203	2.5	199	1.7
10	243	8.4	235	9.7
11	278	2.1	272	5.0
12	294	13.8	291	4.4
13	332	8.4	321	5.7
14	335	4.6	327	1.4
15	347	1.3	334	0.8
16	364	6.3	349	2.7
17	402	11.3	387	3.4
18	417	25.1	399	36.7
19	421	19.6	461	38.9
20	528	139.6	509	272.8
21	546	248.3	525	118.4
22	591	5.0	553	2.8
23	614	446.6	589	491.1
24	637	40.9	633	106.4
25	733	101.7	698	114.7
26	815	32.7	780	50.3
27	867	59.2	833	68.4
28	972	171.1	936	189.1
29	1216	164.6	1213	366.2
30	1225	141.8	1237	338.7
31	1268	905.0	1277	651.0
32	1340	590.0	1331	661.2
33	3570	117.1	3565	105.3

Section 3. Bond lengths for chemical species appearing in the ring-opening reaction at the MP2/aTZ level of theory

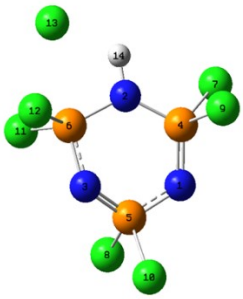
Table S16. Bond lengths (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



Type	Bond Length	Type	Bond Length
P6-N2	1.60492	P5-Cl10	2.00553
N2-P4	1.60492	Cl13-H14	1.29704
P4-N1	1.59291	H14-N2	1.88757
N1-P5	1.59715	Cl13-P6	4.21028
P5-N3	1.59715	Cl13-P4	4.21024
N3-P6	1.59291	H14-Cl11	3.68898
P6-Cl11	2.00432	H14-Cl12	3.43476
P6-Cl12	2.00247	H14-Cl7	3.68895
P4-Cl7	2.00432	H14-Cl9	3.43473
P4-Cl9	2.00246	H14-P6	3.01860
P5-Cl8	2.00545		

Color code: P = orange, N = blue, Cl = green, H = white

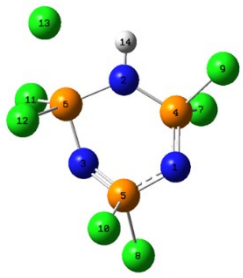
Table S17. Bond lengths (in Angstrom, Å) of the first transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



Type	Bond Length	Type	Bond Length
P6-N2	1.68347	P5-Cl10	1.99772
N2-P4	1.65275	Cl13-H14	1.95737
P4-N1	1.57166	H14-N2	1.04645
N1-P5	1.61854	Cl13-P6	2.68283
P5-N3	1.57072	Cl13-P4	4.27933
N3-P6	1.62286	H14-Cl11	3.40361
P6-Cl11	2.00224	H14-Cl12	3.40152
P6-Cl12	1.99008	H14-Cl7	3.03531
P4-Cl7	1.98654	H14-Cl9	3.41759
P4-Cl9	2.00436	H14-P6	2.25442
P5-Cl8	2.01261	H14-P4	2.40052

Color code: P = orange, N = blue, Cl = green, H = white

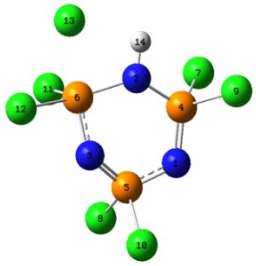
Table S18. Bond lengths (in Angstrom, Å) of the intermediate (**Int'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



Type	Bond Length	Type	Bond Length
P6-N2	1.71645	P5-Cl10	2.01748
N2-P4	1.66359	Cl13-H14	2.27058
P4-N1	1.57293	H14-N2	1.01644
N1-P5	1.63370	Cl13-P6	2.25387
P5-N3	1.56105	Cl13-P4	4.30166
N3-P6	1.66211	H14-Cl11	3.66972
P6-Cl11	2.03388	H14-Cl12	3.73229
P6-Cl12	2.04885	H14-Cl7	3.41412
P4-Cl7	2.01159	H14-Cl9	2.86459
P4-Cl9	1.98868	H14-P6	2.34223
P5-Cl8	2.00428	H14-P4	2.32156

Color code: P = orange, N = blue, Cl = green, H = white

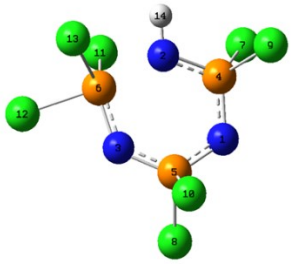
Table S19. Bond lengths (in Angstrom, Å) of the second transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



Type	Bond Length	Type	Bond Length
P6-N2	1.77729	P5-Cl10	2.00101
N2-P4	1.64552	Cl13-H14	2.22487
P4-N1	1.56780	H14-N2	1.01675
N1-P5	1.62028	Cl13-P6	2.20629
P5-N3	1.56329	Cl13-P4	4.24016
N3-P6	1.63749	H14-Cl11	3.40552
P6-Cl11	2.03755	H14-Cl12	4.13039
P6-Cl12	2.08601	H14-Cl7	3.07201
P4-Cl7	2.00800	H14-Cl9	3.09573
P4-Cl9	2.00396	H14-P6	2.36822
P5-Cl8	2.01592	H14-P4	2.26789

Color code: P = orange, N = blue, Cl = green, H = white

Table S20. Bond lengths (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



Type	Bond Length	Type	Bond Length
P6-N2	1.88805	P5-Cl10	2.01753
N2-P4	1.62021	Cl13-H14	2.54694
P4-N1	1.58015	H14-N2	1.01557
N1-P5	1.60972	Cl13-P6	2.06180
P5-N3	1.58080	Cl13-P4	4.24511
N3-P6	1.60390	H14-Cl11	2.99808
P6-Cl11	2.06451	H14-Cl12	4.44028
P6-Cl12	2.12193	H14-Cl7	3.29396
P4-Cl7	2.00986	H14-Cl9	3.01365
P4-Cl9	2.00937	H14-P6	2.47413
P5-Cl8	1.99476	H14-P4	2.25161

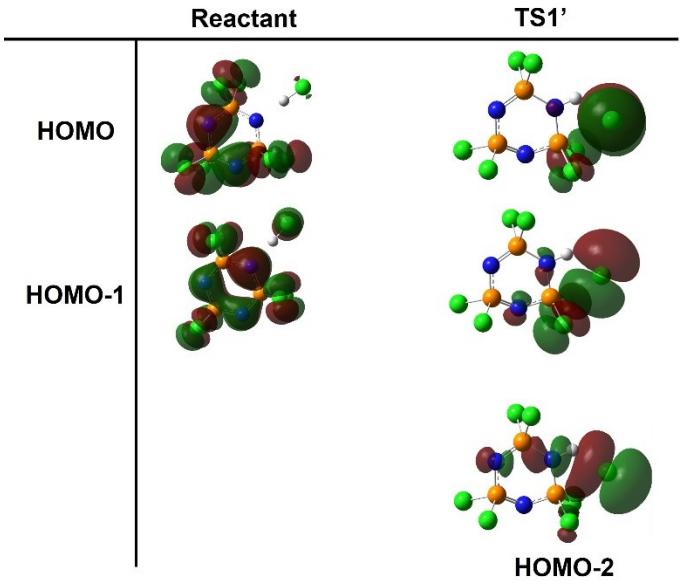
Color code: P = orange, N = blue, Cl = green, H = white

Section 4. The energies and shapes of the frontier molecular orbitals of selected structures

Table S21. The energy (in Hartree) of selected frontier molecular orbitals of the reactant (**R**) and transition state (**TS1'**) in the ring-opening reaction at the MP2/aTZ level of theory

Selected Frontier Molecular Orbital	R'	TS1'
LUMO	0.037	0.028
HOMO	-0.442	-0.378
HOMO-1	-0.443	-0.389
HOMO-2	-0.451	-0.439
HOMO-3	-0.451	-0.463
HOMO-4	-0.464	-0.465
HOMO-5	-0.473	-0.488
HOMO-6	-0.474	-0.493

Figure S1. The shape of the selected frontier molecular orbitals of the reactant (**R**) and transition state (**TS1'**) in the ring-opening reaction at the MP2/aTZ level of theory

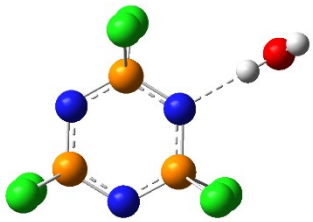


Section 5. Cartesian Coordinates

Section 5.1 Electronic structures fully optimized at the MP2/aTZ level of theory

Section 5.1.1. Cartesian Coordinates for the pivotal structure of the hydrolysis reaction followed by HCl-catalyzed tautomerization calculated at the MP2/aTZ level of theory

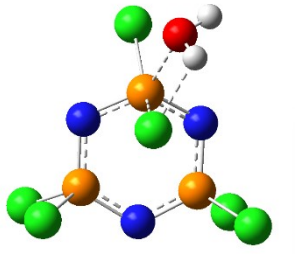
Table S22. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the MP2/aTZ level of theory.



P	0.03953300	0.54806100	1.39141500
P	0.03953300	0.54806100	-1.39141500
P	0.04254100	-1.84871600	0.00000000
N	0.03407400	1.34372000	0.00000000
N	0.03953300	-1.04604100	1.38036000
N	0.03953300	-1.04604100	-1.38036000
Cl	-1.50487000	1.19582600	2.48690100
Cl	-1.51002300	-3.11907400	0.00000000
Cl	1.61029300	1.18439700	-2.46859500
Cl	-1.50487000	1.19582600	-2.48690100
Cl	1.60592000	-3.10726300	0.00000000
Cl	1.61029300	1.18439700	2.46859500
H	-0.13733700	4.76306700	0.00000000
O	-0.89755900	4.17481500	0.00000000
H	-0.51289200	3.28598300	0.00000000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

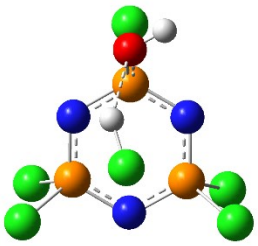
Table S23. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the MP2/aTZ level of theory.



P	0.52690000	1.42957100	-0.17816800
P	1.00705200	-1.23671200	-0.12696700
P	-1.60357200	-0.25186100	-0.07421700
N	1.58073200	0.23927600	-0.40498600
N	-1.05299100	1.22640700	-0.40239400
N	-0.56309500	-1.45878600	0.04577700
Cl	0.82476700	2.67512100	-1.80001000
Cl	-2.91245600	-0.66470400	-1.53937400
Cl	1.93231600	-2.05090800	1.46038500
Cl	1.67647400	-2.40154700	-1.61975600
Cl	-2.79356400	-0.27564500	1.54053200
Cl	0.30829200	1.16571500	2.19172100
H	1.79624400	2.35989500	1.56780900
O	1.67306700	2.75589800	0.66589000
H	2.50187900	2.81312200	0.15711800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

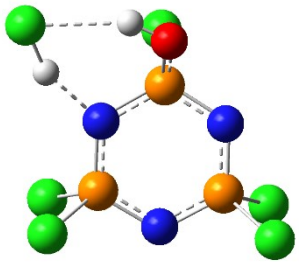
Table S24. Cartesian coordinates (in Angstrom, Å) of the products (**P_1HB**) for the hydrolysis reaction fully optimized at the MP2/aTZ level of theory.



P	0.00200100	-0.98765000	1.39741600
P	-1.42031700	0.21100900	-0.64404400
P	1.34060700	0.05131900	-0.76917200
N	-1.39044300	-0.48907700	0.79098200
N	1.37319600	-0.57046800	0.70250100
N	-0.04737800	0.53993100	-1.38934100
Cl	-0.08898800	-2.99836300	1.57691300
Cl	2.17880600	-1.26194000	-2.04923600
Cl	-2.49799200	1.89412300	-0.50919700
Cl	-2.56004500	-0.89999600	-1.87936500
Cl	2.64141800	1.56776200	-0.83224000
Cl	0.35508600	2.73096400	1.94191400
H	0.68355600	1.63986100	2.52506200
O	0.14151900	-0.50448200	2.91734700
H	-0.67852900	-0.64024200	3.41476600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

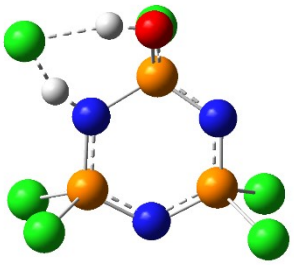
Table S25. Cartesian coordinates (in Angstrom, Å) of the product with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the MP2/aTZ level of theory.



P	0.58834700	1.36484900	-0.16510200
P	-1.91794700	0.21854900	-0.26560500
P	0.29633900	-1.37830400	0.22124200
N	-0.96452600	1.47346500	-0.49256900
N	1.24197500	-0.10936600	-0.02918600
N	-1.27918700	-1.21062400	0.06678300
Cl	0.97937300	2.35114600	1.55508100
Cl	0.68242100	-2.14572600	2.03956800
Cl	-3.09570000	0.03093600	-1.87532200
Cl	-3.25151400	0.64590700	1.17639800
Cl	0.93540000	-2.84661100	-0.98416600
Cl	4.11629000	0.57365300	-0.84559900
H	3.00401600	0.02180800	-0.41850400
O	1.36906400	2.18461700	-1.26480200
H	2.32795100	1.99234300	-1.25763800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

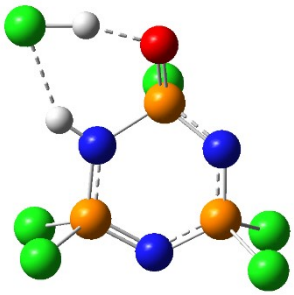
Table S26. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the MP2/aTZ level of theory.



P	-0.49031500	-1.49845900	-0.18118600
P	1.86917800	-0.05640400	-0.30855500
P	-0.45954900	1.33337300	0.35752800
N	1.00968000	-1.34107200	-0.67490200
N	-1.26301900	-0.05850900	0.11394600
N	1.11423600	1.24431100	0.25083800
Cl	-0.51346600	-2.53039200	1.54285500
Cl	-0.95506300	2.06663400	2.14552800
Cl	2.93813900	0.45374700	-1.91712200
Cl	3.28905100	-0.52300000	1.02733000
Cl	-1.24379400	2.66855400	-0.89763200
Cl	-3.75729400	-0.68437200	-1.01452100
H	-2.36434400	-0.11842200	-0.25238200
O	-1.37579400	-2.28401000	-1.17821200
H	-2.32402300	-1.87015800	-1.23734700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S27. Cartesian coordinates (in Angstrom, Å) of the final product (**P** fully optimized at the MP2/aTZ level of theory) after the HCl-catalyzed tautomerization.

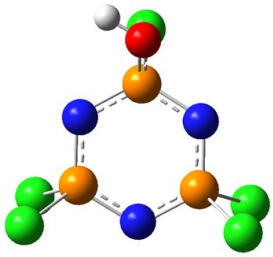


P	-0.63430500	-1.47049700	-0.24536600
P	1.86961000	-0.26177000	-0.34296500
P	-0.27624000	1.42537100	0.25264000
N	0.87003200	-1.39838200	-0.79030000
N	-1.21443700	0.14717200	-0.14334200
N	1.26391500	1.13111700	0.20047400
Cl	-0.54686300	-2.02845600	1.71492600
Cl	-0.78661600	2.10630400	2.06205500
Cl	3.09071600	0.14335200	-1.87277600
Cl	3.14632000	-0.89572400	1.07149900
Cl	-0.83592400	2.93055400	-0.93614500
Cl	-4.20270800	-0.78170500	-0.90801500
H	-2.22918500	0.25142200	-0.23590700
O	-1.63991300	-2.28290300	-0.97658100
H	-3.17779900	-1.60762600	-1.02016700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.1.2. Cartesian coordinates for chemical species appearing in tautomerization reaction in the absence of HCl interference calculated at the MP2/aTZ level of theory

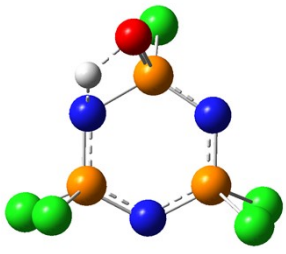
Table S28. Cartesian coordinates (in Angstrom, Å) of the reactants in the tautomerization reaction occurring in the absence of HCl interferences (**Tauto_R**) fully optimized at the MP2/aTZ level of theory.



P	0.02573400	1.65260800	-0.63291400
P	-1.40252500	-0.60161700	0.03796800
P	1.36590700	-0.66577700	0.03621800
N	-1.36881600	0.88887500	-0.52604900
N	1.39227800	0.82105400	-0.53939200
N	-0.03469400	-1.38392600	0.30589000
Cl	0.09650700	3.10542900	0.77855100
Cl	2.44342200	-0.74510800	1.73521100
Cl	-2.54182800	-1.70506600	-1.19144300
Cl	-2.48142400	-0.64095700	1.73568700
Cl	2.46007300	-1.82376900	-1.18611500
O	-0.02260900	2.47327500	-1.99298600
H	0.81803200	2.91457600	-2.18048200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S29. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without HCl interferences (**Tauto_TS**) fully optimized at the MP2/aTZ level of theory.

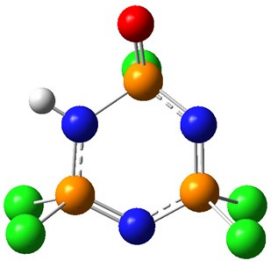


P	-0.23069100	1.71131600	-0.65901600
P	-1.31848200	-0.74340700	0.04551900
P	1.44341100	-0.46303300	0.20534400
N	-1.45670100	0.69159000	-0.61860500
N	1.29353300	1.06356700	-0.31008000
N	0.10799300	-1.21983100	0.60868900
Cl	-0.64256800	3.19746800	0.62473700
Cl	2.67651200	-0.53182200	1.77669200
Cl	-2.00077200	-2.11212100	-1.25554900
Cl	-2.61459700	-0.92667300	1.56367500
Cl	2.48351200	-1.46232100	-1.19505300
O	0.28758900	2.28192900	-1.98818000
H	1.33647700	1.62711800	-1.47882900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S30. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without HCl interferences (**Tauto_P**) fully optimized at the MP2/aTZ level of theory.

fully optimized structure

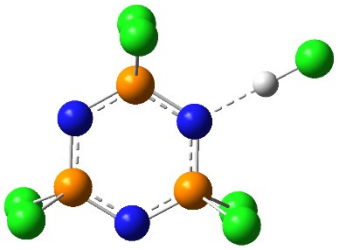


P	-0.19787300	1.69858500	-0.97782200
P	-1.37586700	-0.63454100	0.00388200
P	1.41320300	-0.56829100	0.08330700
N	-1.39325600	0.62352300	-0.94251400
N	1.26514400	0.76889800	-0.84735600
N	0.04805000	-1.20613700	0.51140500
Cl	-0.22318000	2.65630200	0.83756700
Cl	2.53106700	-0.16080100	1.69484100
Cl	-2.34521700	-2.13001800	-0.90496000
Cl	-2.47548900	-0.36230300	1.66447500
Cl	2.59119400	-1.83525700	-0.92279100
O	-0.05746900	2.64793700	-2.09416600
H	2.09587500	1.22152600	-1.21316800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.1.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the MP2/aTZ level of theory

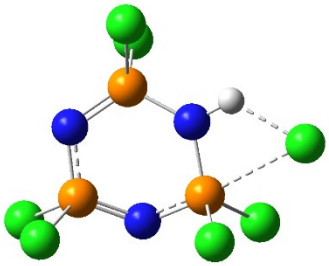
Table S31. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



N	1.25220000	-1.38016100	-0.03058100
N	-1.13106100	0.00001600	0.10000700
N	1.25222700	1.38014500	-0.03059300
P	-0.33761200	-1.39467100	0.06757700
P	2.05427900	-0.00001600	-0.08299700
P	-0.33758400	1.39468600	0.06757100
Cl	-0.88438200	-2.46223700	1.67339200
Cl	3.41435900	-0.00002300	1.39077500
Cl	-1.08198300	-2.48953800	-1.43476900
Cl	3.21373400	-0.00003500	-1.71939400
Cl	-0.88432600	2.46226800	1.67338600
Cl	-1.08193900	2.48956600	-1.43477400
Cl	-4.30066200	-0.00000100	-0.20680800
H	-3.01141900	0.00001600	-0.06481400

Color code: P = orange, N = blue, Cl = green, H = white

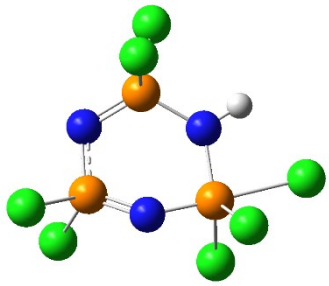
Table S32. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



N	1.75305600	0.78200700	-0.35623200
N	-0.97110400	0.83718600	-0.05749600
N	0.30871900	-1.32447300	0.60435600
P	0.46509900	1.65231900	-0.12423200
P	1.66390800	-0.79048200	0.01658200
P	-1.18253500	-0.80892400	0.22482100
Cl	0.22602000	2.99127800	-1.57211900
Cl	2.26818100	-1.78642200	-1.62462500
Cl	0.59277200	2.79210000	1.51956600
Cl	3.11630500	-1.20129400	1.32527300
Cl	-1.65207400	-1.93585700	-1.36216100
Cl	-2.14541900	-1.36808400	1.87424500
Cl	-3.57814600	0.26534900	-0.32704000
H	-1.90164800	1.27307300	-0.25534900

Color code: P = orange, N = blue, Cl = green, H = white

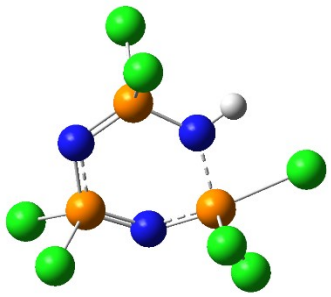
Table S33. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



N	-1.88100600	0.33218400	-0.58585900
N	0.74051200	1.14186800	-0.29647000
N	0.06924500	-1.08315300	0.66572300
P	-0.88336100	1.49956800	-0.24523100
P	-1.34546500	-1.09329200	0.00589800
P	1.47089100	-0.33947300	0.17082300
Cl	-1.24803200	2.38299200	1.52481700
Cl	-2.66751200	-1.73153400	1.37044600
Cl	-1.07734900	2.99100700	-1.54632300
Cl	-1.62118300	-2.41551700	-1.49274700
Cl	2.32641900	-0.54108800	2.00496800
Cl	1.97037300	-1.75848100	-1.22012300
Cl	3.34588600	0.74253200	-0.45656300
H	1.38151100	1.87318000	-0.59220600

Color code: P = orange, N = blue, Cl = green, H = white

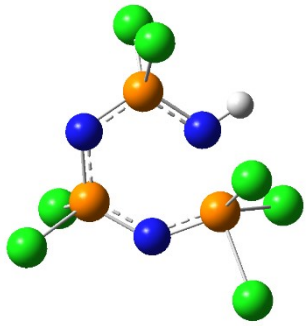
Table S34. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



N	1.96606400	0.10796600	0.05777200
N	-0.36429000	-1.28199200	-0.31846800
N	-0.47970200	1.23780500	-0.47028800
P	1.26195900	-1.28722600	-0.06745200
P	1.02368200	1.41860400	-0.08167900
P	-1.54618400	0.03546900	-0.15664200
Cl	1.61777600	-2.42574600	1.54785600
Cl	1.24689800	2.45133000	1.63517700
Cl	2.05745100	-2.40676900	-1.52678900
Cl	1.89655200	2.62666300	-1.41687400
Cl	-1.89216000	0.16493100	1.84714100
Cl	-3.04990700	1.18850800	-1.02885100
Cl	-2.94434900	-1.64281900	-0.46682100
H	-0.79480100	-2.20283000	-0.34079400

Color code: P = orange, N = blue, Cl = green, H = white

Table S35. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the MP2/aTZ level of theory.



N	-1.74714600	0.50636600	-0.54606000
N	-0.02819500	-1.18104300	0.61868900
N	0.89068000	1.15690500	-0.03619800
P	-1.49428700	-0.96811100	-0.03729700
P	-0.62380800	1.59273000	-0.15991000
P	1.56297700	-0.28974600	0.13032100
Cl	-1.90870100	-2.23911200	-1.53808300
Cl	-0.75374600	3.02653500	-1.54063600
Cl	-2.81862300	-1.55945000	1.35339900
Cl	-1.17561000	2.55470900	1.52548200
Cl	1.74096900	-1.61630200	-1.44154600
Cl	3.49118600	0.48520100	-0.29870300
Cl	2.27085600	-1.02270700	1.92272500
H	0.13179600	-2.08954500	1.04342700

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.2 Coordinates for the electronic structures fully optimized at the B3LYP/6-311+G(d,p) level of theory

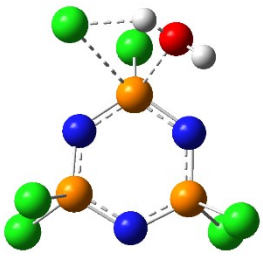
Section 5.2.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the B3LYP/6-311+G(d,p) level of theory

Table S36. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.

P	0.60567900	-1.37539400	-0.01924300
P	0.50907800	1.44033800	-0.00051200
P	-1.86926600	-0.05100500	0.01820000
N	1.32842000	0.05898600	-0.01653300
N	-0.98730700	-1.38092900	0.00206400
N	-1.08049600	1.33626600	0.02184400
Cl	1.31125400	-2.47316000	1.53704100
Cl	-3.13475600	-0.10587700	1.61177600
Cl	1.08873400	2.56181600	-1.60070300
Cl	1.13955300	2.56406400	1.56931200
Cl	-3.16018400	-0.08414400	-1.55702500
Cl	1.26160600	-2.43387500	-1.63276800
H	4.69640200	0.17970000	-0.62710500
O	4.34265800	0.16077700	0.26681900
H	3.38131300	0.12797100	0.15541800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

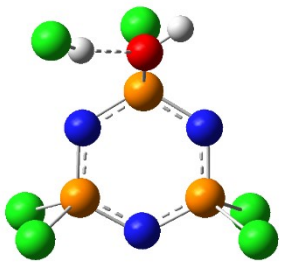
Table S37. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-1.14271900	-0.89419700	0.23787600
P	1.66803400	-0.68729500	-0.19931900
P	0.16437800	1.62487500	0.10701500
N	0.30707200	-1.52573700	-0.11468300
N	-1.05761600	0.67986200	0.52053700
N	1.55659500	0.90215900	-0.20846600
Cl	-2.01903200	-1.70991100	1.85980100
Cl	0.41229100	2.96344000	1.61282200
Cl	2.66582100	-1.28468000	-1.87228200
Cl	2.93366700	-1.28988200	1.28762100
Cl	-0.32474200	2.81130200	-1.47343600
Cl	-3.50062600	-0.21300600	-1.03004700
H	-2.68693400	-1.80302600	-1.30832600
O	-1.86900800	-2.29865700	-0.90527100
H	-1.19418300	-2.56594900	-1.55094300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

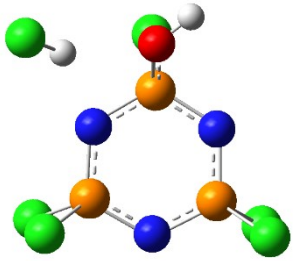
Table S38. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-0.68409800	-1.11683300	0.64573200
P	1.75437200	-0.53717700	-0.59282300
P	0.05794800	1.54109400	0.23739400
N	0.65460500	-1.58218400	-0.09520900
N	-0.99960800	0.44135600	0.70766800
N	1.42514800	1.01110900	-0.39531200
Cl	-0.69669800	-1.92017400	2.52971000
Cl	0.49504900	2.78052000	1.79562200
Cl	2.15980500	-0.90096600	-2.55812400
Cl	3.54790200	-0.94682700	0.28863500
Cl	-0.85241200	2.80436000	-1.07295000
Cl	-4.83788800	-0.59964400	-1.26041000
H	-3.69616700	-0.87820700	-0.71981200
O	-1.96988400	-1.80638900	-0.03410200
H	-1.89700400	-2.76245500	-0.16418900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

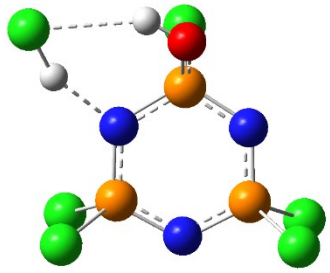
Table S39. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-0.48282900	-1.41171600	0.26995400
P	1.88693300	-0.16209700	-0.52825000
P	-0.26642300	1.36776100	0.42517300
N	0.98339300	-1.46762100	-0.36479400
N	-1.12562500	0.02461000	0.52951300
N	1.23585500	1.22946800	-0.09796800
Cl	-0.47989800	-2.52226000	1.99392300
Cl	-0.24364700	2.31730700	2.22964800
Cl	2.52587000	-0.04610800	-2.46202000
Cl	3.64371800	-0.40375700	0.47963100
Cl	-1.27886800	2.69018100	-0.74245700
Cl	-4.61211900	-0.51283700	-1.26893900
H	-3.42844500	-0.77240500	-0.82482200
O	-1.54967000	-2.17922100	-0.64644300
H	-1.33072400	-3.09119900	-0.88042600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

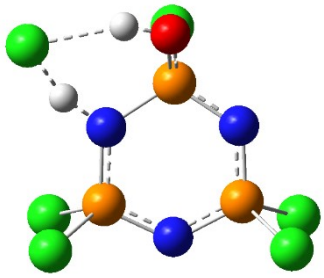
Table S40. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-0.56128700	-1.41307400	-0.13318300
P	1.95182700	-0.19236400	-0.25616100
P	-0.32225400	1.37065300	0.26562900
N	1.00317600	-1.45998000	-0.40978500
N	-1.22040800	0.06000800	0.03576300
N	1.25094300	1.19850000	0.10640200
Cl	-0.99408400	-2.49657500	1.54981100
Cl	-0.72099300	2.18166400	2.09565800
Cl	3.04462700	0.02884500	-1.96000700
Cl	3.39500900	-0.56837900	1.13220800
Cl	-0.99997100	2.82136800	-0.99293900
Cl	-4.16776700	-0.52032900	-0.89304300
H	-3.05399400	-0.00681300	-0.40484400
O	-1.30064300	-2.19743800	-1.29764000
H	-2.26708400	-2.07372300	-1.32365700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

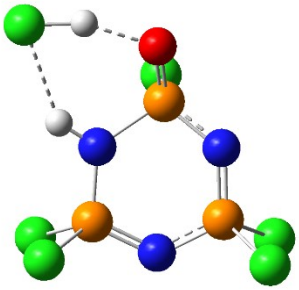
Table S41. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-0.52434800	-1.50407800	-0.14670700
P	1.90950700	-0.10736600	-0.28214400
P	-0.43125000	1.35395600	0.33061800
N	1.01781800	-1.40398100	-0.49273900
N	-1.25895000	-0.01986500	0.03455800
N	1.13634500	1.21357900	0.19004800
Cl	-0.76206000	-2.53371600	1.59409300
Cl	-0.89180800	2.06258300	2.17562900
Cl	2.93442300	0.28012100	-1.99183900
Cl	3.39680900	-0.47383400	1.05334700
Cl	-1.18717700	2.77171000	-0.89877800
Cl	-3.78931800	-0.60198400	-1.06074600
H	-2.42825300	-0.08040700	-0.35160800
O	-1.34610600	-2.27967100	-1.22417100
H	-2.29277900	-1.93101100	-1.32359300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S42. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the B3LYP/6-311+G(d,p) level of theory.



P	-0.69346600	-1.49062400	-0.11612100
P	1.88770600	-0.32426400	-0.37399400
P	-0.19873100	1.46269900	0.29588400
N	0.82271600	-1.45368400	-0.62388100
N	-1.19613500	0.17943100	0.03417500
N	1.31387300	1.08754800	0.15550800
Cl	-0.67104100	-2.13865400	1.84732400
Cl	-0.56446900	2.28297300	2.11698800
Cl	2.94315300	-0.00218100	-2.07997600
Cl	3.33701900	-0.89250000	0.93927200
Cl	-0.79649000	2.93402900	-0.97183600
Cl	-4.37080800	-0.68289600	-1.01925600
H	-2.20429900	0.32765800	-0.03545600
O	-1.73226900	-2.21394700	-0.88529400
H	-3.36857300	-1.53943900	-1.08213200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.2.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the B3LYP/6-311+G(d,p) level of theory

Table S43. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the B3LYP/6-311+G(d,p) level of theory.

P	0.02969900	1.68938500	-0.58213700
P	-1.42185900	-0.60723400	0.05705100
P	1.38039400	-0.67927500	0.05383900
N	-1.35026400	0.91066400	-0.41958400
N	1.37909900	0.83539900	-0.44161100
N	-0.03814500	-1.36724800	0.30251600
Cl	0.11133200	3.24094200	0.76115500
Cl	2.50249500	-0.86133600	1.75123700
Cl	-2.54263500	-1.66551300	-1.27885700
Cl	-2.54902700	-0.74355200	1.75243300
Cl	2.45381900	-1.80090300	-1.27213900
O	-0.01796300	2.43863800	-1.99203100
H	0.79364300	2.91219600	-2.21939200

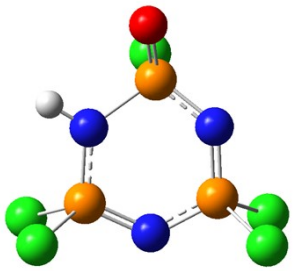
Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S44. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the B3LYP/6-311+G(d,p) of theory.

P	-0.16104700	1.74140500	-0.66971500
P	-1.38464400	-0.68839600	0.03873400
P	1.43696900	-0.55791000	0.15792400
N	-1.42999800	0.78697900	-0.54453700
N	1.32710800	0.95069100	-0.42526100
N	0.04918700	-1.25561600	0.47650900
Cl	-0.39930700	3.27336300	0.64440600
Cl	2.58161300	-0.61513500	1.84001800
Cl	-2.24035000	-1.96398700	-1.30059400
Cl	-2.62264100	-0.85696300	1.64550100
Cl	2.55192500	-1.63503000	-1.16531300
O	0.35222100	2.27588600	-2.01899900
H	1.37789200	1.55383300	-1.58740900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S45. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the B3LYP/6-311+G(d,p) level of theory.

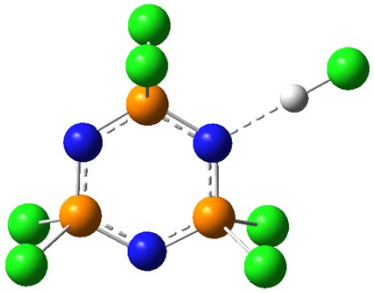


P	-0.22343300	1.75797100	-0.93133100
P	-1.38752400	-0.66252700	0.03249200
P	1.43463200	-0.57064600	0.10442300
N	-1.39841500	0.67269500	-0.79061300
N	1.26961600	0.83949200	-0.72639200
N	0.06153400	-1.20119800	0.50372400
Cl	-0.25519600	2.90073600	0.80545000
Cl	2.60651500	-0.29668400	1.74483800
Cl	-2.30057500	-2.13018000	-1.03911200
Cl	-2.53973400	-0.57071800	1.71305800
Cl	2.58989400	-1.79655500	-1.04101600
O	-0.08644200	2.60578300	-2.12421200
H	2.09189500	1.29266500	-1.11179000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.2.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at B3LYP/6-311+G(d,p) level of theory

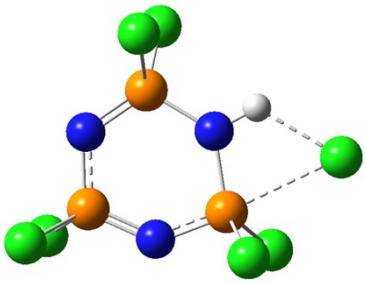
Table S46. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



N	0.00001900	-1.24890300	1.35835700
N	0.00005400	1.11538200	0.00000000
N	0.00001900	-1.24890300	-1.35835700
P	0.00001900	0.34211900	1.41130100
P	-0.00009500	-2.08664900	0.00000000
P	0.00001900	0.34211900	-1.41130100
Cl	1.58504800	0.98757600	2.50911800
Cl	1.58443700	-3.36384900	0.00000000
Cl	-1.58504600	0.98762000	2.50905200
Cl	-1.58494300	-3.36347800	0.00000000
Cl	1.58504800	0.98757600	-2.50911800
Cl	-1.58504600	0.98762000	-2.50905200
Cl	0.00049500	4.40151100	0.00000000
H	0.00032700	3.09534900	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

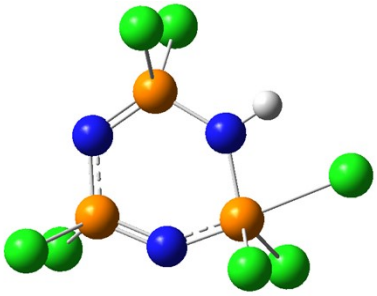
Table S47. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



N	-1.92355900	-0.13250200	0.00000000
N	0.44978800	1.20159900	0.00000000
N	0.44568400	-1.39490600	0.00000000
P	-1.21703000	1.26090800	0.00000000
P	-1.10450200	-1.52745100	0.00000000
P	1.49280300	-0.16421700	0.00000000
Cl	-1.76277000	2.40671400	1.58310700
Cl	-1.76277000	-2.62500600	1.58447800
Cl	-1.76277000	2.40671400	-1.58310700
Cl	-1.76277000	-2.62500600	-1.58447800
Cl	2.53725000	-0.59662000	1.70245500
Cl	2.53725000	-0.59662000	-1.70245500
Cl	3.07171600	2.02214200	0.00000000
H	1.01023900	2.07263700	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

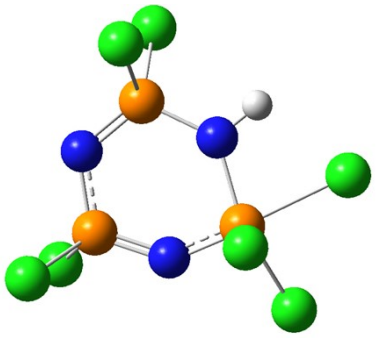
Table S48. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



N	-1.86507000	0.52496700	-0.00048500
N	0.81384400	1.05811900	-0.00022400
N	0.02258700	-1.37900200	0.00116700
P	-0.75792800	1.62165400	-0.00021500
P	-1.48776200	-1.05560200	0.00012600
P	1.44211400	-0.57101600	0.00033400
Cl	-0.91448000	2.89071800	1.58185900
Cl	-2.46188200	-1.89921000	1.58369600
Cl	-0.91416000	2.89106300	-1.58200200
Cl	-2.46031400	-1.89987500	-1.58412500
Cl	2.15141200	-1.42597200	1.75383900
Cl	2.15046600	-1.42734700	-1.75292400
Cl	3.49000900	0.68757800	-0.00071000
H	1.55624900	1.75761900	-0.00061900

Color code: P = orange, N = blue, Cl = green, H = white

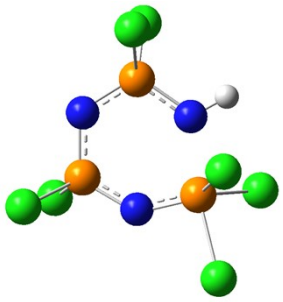
Table S49. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



N	-1.95387000	-0.00781100	-0.03721500
N	0.43744300	1.27432000	-0.14777100
N	0.42424300	-1.28019600	-0.10038100
P	-1.21000200	1.36711500	-0.06682600
P	-1.12465000	-1.39671500	-0.04370600
P	1.56903700	-0.12997700	-0.01738800
Cl	-1.71247400	2.52826600	1.53361000
Cl	-1.73425400	-2.47898800	1.57470500
Cl	-1.80729100	2.53122700	-1.62794200
Cl	-1.82748100	-2.51199200	-1.59699900
Cl	2.14980100	-0.15334600	1.96575900
Cl	2.94874800	-1.42266700	-1.00597200
Cl	3.05367300	1.52694200	-0.59785900
H	0.92723800	2.15894200	-0.25376300

Color code: P = orange, N = blue, Cl = green, H = white

Table S50. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/6-311+G(d,p) level of theory.



N	-1.74198500	0.69383000	-0.22504500
N	-0.15304100	-1.36242200	0.36486800
N	0.95607500	1.00786900	0.02896300
P	-1.64409800	-0.86315000	0.00486500
P	-0.47770200	1.65911300	-0.06126000
P	1.57772000	-0.45621100	0.07664800
Cl	-2.43386300	-1.82851900	-1.62196300
Cl	-0.51443900	2.97400400	-1.60777700
Cl	-2.91012300	-1.48813800	1.48582500
Cl	-0.75320900	2.86810700	1.55879300
Cl	1.76895700	-1.66964600	-1.62917200
Cl	3.59677300	0.27129000	-0.16652400
Cl	2.11552000	-1.42875800	1.85800000
H	-0.04961400	-2.34299900	0.60262500

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.3 Electronic structures fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory

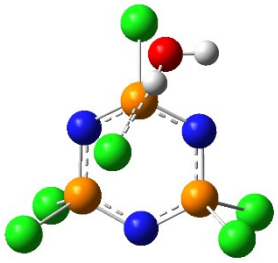
Section 5.3.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the B3LYP-D3/6-311+G(d,p) level of theory

Table S51. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	0.62042300	-1.37212500	-0.02039400
P	0.52474700	1.43702100	-0.00212700
P	-1.84489400	-0.05010900	0.02059600
N	1.34066300	0.05868000	-0.02211700
N	-0.96935000	-1.38116600	0.01000300
N	-1.06195000	1.33746900	0.02654000
Cl	1.33514600	-2.45838300	1.53179500
Cl	-3.10800100	-0.10302200	1.60891700
Cl	1.10016200	2.54695200	-1.60462400
Cl	1.16361300	2.54856200	1.56526400
Cl	-3.12008100	-0.08384500	-1.56122600
Cl	1.26833400	-2.41879000	-1.63778300
H	4.61530700	0.17797400	-0.62229400
O	4.26544800	0.16005100	0.27302200
H	3.30312300	0.12626400	0.16301300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

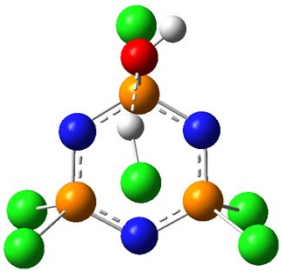
Table S52. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.



P	0.63435900	-1.37994800	0.36928500
P	0.89790900	1.34572200	0.10344200
P	-1.64263800	0.14614400	0.03805900
N	1.54571600	-0.07368300	0.50453100
N	-0.95503300	-1.24776800	0.47917100
N	-0.67182400	1.39619400	-0.13682900
Cl	0.99180100	-2.66208500	1.91187600
Cl	-3.00134500	0.54794700	1.49611300
Cl	1.84520900	2.10903100	-1.51699000
Cl	1.41045200	2.65578900	1.57084300
Cl	-2.80501800	-0.04903000	-1.60110700
Cl	0.40675200	-1.30285700	-2.28666300
H	1.88944300	-2.24111900	-1.50857100
O	2.12081000	-2.49740600	-0.56478000
H	2.95415600	-2.06110700	-0.32231200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S53. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.



P	0.00661000	1.18385800	1.24762800
P	1.42246200	-0.28978100	-0.64767800
P	-1.36760300	-0.16739400	-0.75240300
N	1.37832700	0.61925000	0.66155400
N	-1.35274100	0.68339400	0.59734300
N	0.02970400	-0.69653000	-1.30427600
Cl	0.09826700	3.22769200	1.23460800
Cl	-2.27354300	0.92863100	-2.21754800
Cl	2.49845100	-1.96476400	-0.26057900
Cl	2.56568700	0.63490100	-2.06246900
Cl	-2.63958600	-1.72544600	-0.53185700
Cl	-0.28418000	-2.38986900	2.29925000
H	-0.45998300	-1.23145300	2.84540700
O	-0.10969800	0.85107100	2.82015100
H	0.62188200	1.19039800	3.35394300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S54. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	-0.50436700	-1.43809000	0.36191000
P	1.77870600	-0.16143700	-0.58899900
P	-0.33544800	1.33582400	0.47444500
N	0.90662500	-1.48034000	-0.38243200
N	-1.15721200	-0.01895400	0.65501300
N	1.13595700	1.22035000	-0.12950600
Cl	-0.35368800	-2.52169900	2.08856500
Cl	-0.22135600	2.30266000	2.26030800
Cl	2.30854100	-0.04265100	-2.54920300
Cl	3.58010600	-0.37809400	0.33337400
Cl	-1.43629000	2.60849900	-0.65298500
Cl	-4.08400700	-0.16991800	-1.55747800
H	-3.15568100	-0.83735500	-0.95792000
O	-1.61640800	-2.23603800	-0.47490200
H	-1.36795700	-3.12264900	-0.76846500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S55. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	-0.55176000	-1.41005200	-0.18527100
P	1.93647000	-0.17079800	-0.26819300
P	-0.34771500	1.35903500	0.26446000
N	1.00109800	-1.43195200	-0.51142700
N	-1.22970500	0.05383800	-0.02978900
N	1.22588100	1.20354900	0.12705400
Cl	-0.90279100	-2.43772300	1.54677700
Cl	-0.78077700	2.08494000	2.11581700
Cl	3.07737600	0.11938000	-1.92068200
Cl	3.32241700	-0.59870600	1.15761200
Cl	-1.02069100	2.83717400	-0.95218900
Cl	-4.09201200	-0.56412600	-0.89502900
H	-2.96283500	-0.03638700	-0.43213200
O	-1.31868200	-2.22908900	-1.30068200
H	-2.28341000	-2.07769900	-1.31741700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S56. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	-0.50041800	-1.49465200	-0.20072800
P	1.89665100	-0.07826300	-0.30208200
P	-0.45619200	1.33334200	0.33886200
N	1.01770900	-1.35867600	-0.62780200
N	-1.26243200	-0.03381200	-0.00855200
N	1.11272200	1.21436700	0.22058000
Cl	-0.61813100	-2.47150000	1.58032700
Cl	-0.94984300	1.97096800	2.19484800
Cl	2.97078700	0.40426700	-1.94773900
Cl	3.32817000	-0.52143700	1.06651600
Cl	-1.21129800	2.76934100	-0.86185800
Cl	-3.79268600	-0.65474900	-1.04471900
H	-2.43882200	-0.11001100	-0.37332300
O	-1.34962900	-2.31567400	-1.21750400
H	-2.29973400	-1.97128200	-1.30239800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S57. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	-0.65243600	-1.48724800	-0.21118500
P	1.88334100	-0.28254300	-0.35959400
P	-0.25908900	1.43538200	0.27976000
N	0.85259800	-1.40787700	-0.74379600
N	-1.21444900	0.15495000	-0.09733300
N	1.26422600	1.09551100	0.19825400
Cl	-0.56921700	-2.05292100	1.77566800
Cl	-0.73228600	2.14058600	2.11808300
Cl	3.03868500	0.13057200	-1.97018200
Cl	3.23485800	-0.90406000	1.02562300
Cl	-0.81999300	2.95081300	-0.94191200
Cl	-4.27138900	-0.75464400	-0.96852900
H	-2.22666300	0.27340500	-0.18314200
O	-1.67058900	-2.27620000	-0.94297500
H	-3.27367100	-1.62163000	-1.06639500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.3.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the B3LYP-D3/6-311+G(d,p) level of theory

Table S58. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	0.03171900	1.66093400	-0.65411400
P	-1.41893900	-0.59632700	0.05738500
P	1.37482800	-0.67340200	0.05402800
N	-1.34967800	0.88424300	-0.51975500
N	1.37783600	0.80182400	-0.54397100
N	-0.04026200	-1.34054000	0.35584700
Cl	0.11590200	3.15408600	0.75226300
Cl	2.49181100	-0.74101700	1.75786000
Cl	-2.53352700	-1.73168300	-1.20928300
Cl	-2.53733400	-0.61956800	1.75859700
Cl	2.43550500	-1.87607500	-1.19883800
O	-0.00926000	2.45538200	-2.03545200
H	0.81463400	2.91253800	-2.25089400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S59. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the B3LYP-D3/6-311+G(d,p) of theory.

P	-0.20638300	1.71313200	-0.71705100
P	-1.35183200	-0.72144600	0.03746600
P	1.44998000	-0.49589500	0.18485000
N	-1.43229200	0.70096400	-0.65764100
N	1.30269800	0.99372600	-0.42717000
N	0.08360200	-1.20482500	0.55528500
Cl	-0.54996800	3.19636700	0.62566000
Cl	2.62668900	-0.49219300	1.83627900
Cl	-2.11756100	-2.11077400	-1.23207800
Cl	-2.61880200	-0.81934300	1.62185700
Cl	2.54309100	-1.58504700	-1.14264600
O	0.32015700	2.28925000	-2.04226700
H	1.36557100	1.60689500	-1.58837300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S60. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

P	-0.19780800	1.71185600	-0.99611300
P	-1.39467100	-0.63129700	0.02267800
P	1.42116900	-0.57493200	0.09763100
N	-1.38610300	0.63717200	-0.90206600
N	1.27477600	0.76850100	-0.83629200
N	0.04196800	-1.16642100	0.52535100
Cl	-0.19837500	2.74603900	0.80993200
Cl	2.56775700	-0.17858000	1.72427100
Cl	-2.33870400	-2.14712600	-0.93539800
Cl	-2.52232800	-0.38415900	1.69854200
Cl	2.57378400	-1.88228500	-0.94327100
O	-0.05550100	2.61500700	-2.14553100
H	2.10286600	1.20466400	-1.22695500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.3.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the B3LYP-D3/6-311+G(d,p) level of theory

Table S61. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

N	-0.05127000	-1.23452500	1.35938400
N	-0.00658500	1.12119300	0.00000000
N	-0.05127000	-1.23452500	-1.35938400
P	-0.05127000	0.35332400	1.40888100
P	-0.05139300	-2.06586700	0.00000000
P	-0.05127000	0.35332400	-1.40888100
Cl	1.50117700	1.00712900	2.53185400
Cl	1.53298100	-3.33457000	0.00000000
Cl	-1.66772800	0.99964100	2.45127800
Cl	-1.63795400	-3.33231000	0.00000000
Cl	1.50117700	1.00712900	-2.53185400
Cl	-1.66772800	0.99964100	-2.45127800
Cl	0.60002000	4.23391900	0.00000000
H	0.31982300	2.95343600	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S62. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

N	-1.74648300	0.79055200	-0.21750400
N	0.96851700	0.84065700	-0.05357100
N	-0.29082500	-1.37221700	0.42944200
P	-0.46761600	1.67821100	-0.08327000
P	-1.68538200	-0.80560900	0.02319800
P	1.20846700	-0.83574800	0.15784900
Cl	-0.51227700	2.86692900	1.56105600
Cl	-3.04959400	-1.28997900	1.43612900
Cl	-0.29478900	2.99458000	-1.60001500
Cl	-2.44339500	-1.67489400	-1.65712300
Cl	2.09144300	-1.50223500	1.85854600
Cl	1.72749300	-1.90272600	-1.50151000
Cl	3.64405800	0.29159500	-0.23755400
H	1.87955900	1.31862300	-0.18725100

Color code: P = orange, N = blue, Cl = green, H = white

Table S63. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

N	-1.85904500	0.44990300	-0.36695100
N	0.78947400	1.09421700	-0.17172300
N	0.02948700	-1.23148500	0.52656200
P	-0.80492100	1.58230600	-0.15907000
P	-1.42847600	-1.06820900	0.02615200
P	1.43977000	-0.48029400	0.15373400
Cl	-1.09488400	2.64610700	1.55417100
Cl	-2.70919800	-1.74107300	1.44594600
Cl	-0.92412200	2.98853300	-1.59976300
Cl	-1.91935800	-2.21243400	-1.59435900
Cl	2.30199800	-0.92263000	1.97637900
Cl	1.94222800	-1.71472800	-1.44286200
Cl	3.44372800	0.69184300	-0.33145800
H	1.49829800	1.79899300	-0.36440000

Color code: P = orange, N = blue, Cl = green, H = white

Table S64. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

N	-1.94351300	-0.01529600	0.02277800
N	0.43176000	1.27318100	-0.23982200
N	0.42420000	-1.27222900	-0.30790300
P	-1.20539800	1.35747600	-0.06585900
P	-1.10622800	-1.39409900	-0.06531200
P	1.55260100	-0.12284000	-0.09537900
Cl	-1.60194300	2.51997400	1.55565300
Cl	-1.52722600	-2.44682900	1.62907300
Cl	-1.89065000	2.50622300	-1.59473900
Cl	-1.94987100	-2.52782200	-1.51886500
Cl	1.98902200	-0.21621600	1.92148700
Cl	2.98732200	-1.36783500	-1.04442200
Cl	3.05701900	1.55187000	-0.51357000
H	0.91582400	2.16314200	-0.31559800

Color code: P = orange, N = blue, Cl = green, H = white

Table S65. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP-D3/6-311+G(d,p) level of theory.

N	-1.70361300	0.60981200	-0.43412700
N	-0.11052300	-1.27989300	0.54549700
N	0.93672500	1.06892200	0.06303000
P	-1.57639200	-0.90476100	-0.02221500
P	-0.52035700	1.63938300	-0.11176500
P	1.56414100	-0.39329600	0.13160600
Cl	-2.15508700	-2.05866600	-1.60139800
Cl	-0.52618500	3.01188900	-1.59570200
Cl	-2.92753800	-1.44670500	1.40618900
Cl	-0.99582500	2.74089000	1.53764800
Cl	1.67367000	-1.63459400	-1.55993500
Cl	3.56287500	0.33556600	-0.23120500
Cl	2.19891100	-1.28347600	1.92069500
H	0.00704000	-2.21514400	0.91787400

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.4 Electronic structures fully optimized at the B3LYP/aTZ level of theory

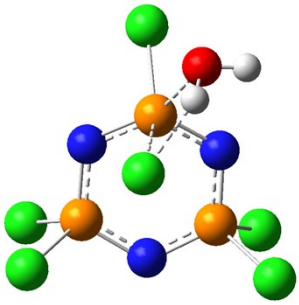
Section 5.4.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the B3LYP/aTZ level of theory

Table S66. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.

P	0.58016600	-1.36580000	-0.00687000
P	0.48435400	1.42860700	0.01138200
P	-1.87847800	-0.05132200	0.01079100
N	1.31544400	0.05833000	-0.00625600
N	-1.01232300	-1.39055900	0.00088500
N	-1.10606400	1.34410500	0.01864800
Cl	1.27219300	-2.45997300	1.55374300
Cl	-3.15712600	-0.10549800	1.58830600
Cl	1.08029400	2.56502800	-1.56549000
Cl	1.10035700	2.54720600	1.58650600
Cl	-3.16284600	-0.08516800	-1.56374100
Cl	1.25179100	-2.43794200	-1.59825100
H	4.79223900	0.18445000	-0.64556500
O	4.41509400	0.16303500	0.23821300
H	3.45759500	0.13103500	0.10628400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

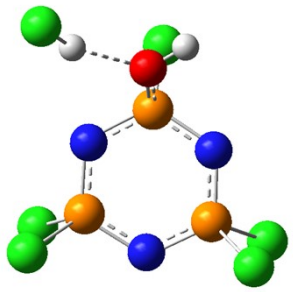
Table S67. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.



P	0.60352300	1.38574500	-0.37459500
P	0.95147000	-1.32976200	-0.01038400
P	-1.61972000	-0.23019600	-0.05398000
N	1.56907500	0.10976000	-0.37653100
N	-0.97782700	1.17255500	-0.51545200
N	-0.62050800	-1.44860800	0.20176500
Cl	0.91498600	2.52777400	-2.04581300
Cl	-2.93256500	-0.73111600	-1.52388200
Cl	1.89060100	-2.07387200	1.62527100
Cl	1.55418400	-2.62726300	-1.45728400
Cl	-2.84732400	-0.03404600	1.54055100
Cl	0.27487100	1.66290400	2.23654100
H	1.74339700	2.46599300	1.39156500
O	2.00711500	2.60645900	0.42394500
H	2.84459300	2.14510000	0.25127200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S68. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.



P	-0.75152400	-0.99570500	0.64687700
P	1.73299400	-0.66710900	-0.55600300
P	0.21819600	1.55870200	0.16836400
N	0.54752800	-1.60799600	-0.05355900
N	-0.94379700	0.58286300	0.65878900
N	1.55395600	0.91168600	-0.41871500
Cl	-0.84954100	-1.72265000	2.55635800
Cl	0.72331000	2.81904500	1.68214900
Cl	2.14517300	-1.12900000	-2.49421000
Cl	3.46639800	-1.20384000	0.36526000
Cl	-0.55670300	2.84699900	-1.19811900
Cl	-5.13164300	-0.52717000	-1.16343000
H	-3.95264200	-0.68686300	-0.66790000
O	-2.07912200	-1.60149800	-0.01615200
H	-2.06206800	-2.56285000	-0.11321400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S69. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.

P	-0.51192900	-1.36680300	0.27471200
P	1.89280800	-0.22160400	-0.52181900
P	-0.19223900	1.38891600	0.39088100
N	0.94987100	-1.49623100	-0.35645800
N	-1.10828400	0.08907800	0.52580400
N	1.30799100	1.20754200	-0.12177100
Cl	-0.55050900	-2.45147100	2.01125800
Cl	-0.15109400	2.37651000	2.16853100
Cl	2.56202400	-0.15850400	-2.44227800
Cl	3.62713300	-0.51775400	0.50119300
Cl	-1.15138300	2.72511600	-0.80011200
Cl	-4.81268600	-0.50115600	-1.19618900
H	-3.60919700	-0.68089200	-0.77725800
O	-1.59750500	-2.11624400	-0.62538400
H	-1.38666500	-3.03610400	-0.83015600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S70. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.

P	-0.58417900	-1.38423600	-0.11396600
P	1.93742700	-0.22023100	-0.25584900
P	-0.28811400	1.37810100	0.26328800
N	0.97601000	-1.47774400	-0.40097800
N	-1.22147600	0.09056100	0.07380600
N	1.28341400	1.19306200	0.10333900
Cl	-1.02955300	-2.47454200	1.55747300
Cl	-0.66447500	2.23752700	2.06948300
Cl	3.02879400	-0.03282300	-1.95948600
Cl	3.38311400	-0.61910600	1.11660400
Cl	-0.94274900	2.81859100	-1.01343700
Cl	-4.19241000	-0.52083100	-0.88725500
H	-3.09546200	0.00446700	-0.38925100
O	-1.34368900	-2.15169200	-1.27136900
H	-2.30394800	-1.98648400	-1.29255100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S71. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the B3LYP/aTZ level of theory.

P	0.02694500	1.68061000	-0.57696200
P	-1.40994200	-0.60789700	0.05519700
P	1.37345800	-0.67150800	0.05477500
N	-1.35708700	0.90969900	-0.42199300
N	1.38461300	0.84505000	-0.43060600
N	-0.03440300	-1.37840300	0.30678300
Cl	0.09763400	3.23318500	0.76004600
Cl	2.50055500	-0.86128100	1.74115900
Cl	-2.53008300	-1.66672900	-1.27321900
Cl	-2.54240800	-0.74786100	1.74067300
Cl	2.44937700	-1.78252200	-1.27072400
O	-0.02172900	2.43274000	-1.98106800
H	0.78879000	2.91409000	-2.19080800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S72. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the B3LYP/aTZ level of theory.

P	-0.16387500	1.73199000	-0.65047200
P	-1.36994400	-0.69332800	0.03708600
P	1.43115200	-0.54768300	0.15822800
N	-1.43903500	0.78488300	-0.53361000
N	1.32839300	0.97306700	-0.38629900
N	0.05845500	-1.27507100	0.47258600
Cl	-0.42451300	3.27392100	0.64292400
Cl	2.58570500	-0.62966300	1.82507300
Cl	-2.22635900	-1.95898800	-1.30345600
Cl	-2.60780800	-0.88252800	1.63604400
Cl	2.54857300	-1.59138700	-1.18070900
O	0.33200400	2.26355900	-2.00284500
H	1.36411800	1.55365900	-1.55649500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.4.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the B3LYP/aTZ level of theory

Table S73. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the B3LYP/aTZ level of theory.

P	-0.22865200	1.75631000	-0.90058500
P	-1.37083200	-0.67561400	0.02968400
P	1.43103900	-0.56525100	0.10322200
N	-1.40788900	0.67914000	-0.75987000
N	1.26396800	0.86868700	-0.67239200
N	0.07195100	-1.23773200	0.48612000
Cl	-0.28830000	2.93703700	0.80084800
Cl	2.59891200	-0.33619500	1.74554600
Cl	-2.29233500	-2.11473300	-1.06357800
Cl	-2.52013200	-0.62451900	1.70746000
Cl	2.60123900	-1.73822800	-1.07036800
O	-0.09261000	2.58443600	-2.10559300
H	2.08180100	1.32503300	-1.05551400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S74. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the B3LYP/aTZ of theory.

P	-0.16387500	1.73199000	-0.65047200
P	-1.36994400	-0.69332800	0.03708600
P	1.43115200	-0.54768300	0.15822800
N	-1.43903500	0.78488300	-0.53361000
N	1.32839300	0.97306700	-0.38629900
N	0.05845500	-1.27507100	0.47258600
Cl	-0.42451300	3.27392100	0.64292400
Cl	2.58570500	-0.62966300	1.82507300
Cl	-2.22635900	-1.95898800	-1.30345600
Cl	-2.60780800	-0.88252800	1.63604400
Cl	2.54857300	-1.59138700	-1.18070900
O	0.33200400	2.26355900	-2.00284500
H	1.36411800	1.55365900	-1.55649500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S75. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the B3LYP/aTZ level of theory.

P	-0.22865200	1.75631000	-0.90058500
P	-1.37083200	-0.67561400	0.02968400
P	1.43103900	-0.56525100	0.10322200
N	-1.40788900	0.67914000	-0.75987000
N	1.26396800	0.86868700	-0.67239200
N	0.07195100	-1.23773200	0.48612000
Cl	-0.28830000	2.93703700	0.80084800
Cl	2.59891200	-0.33619500	1.74554600
Cl	-2.29233500	-2.11473300	-1.06357800
Cl	-2.52013200	-0.62451900	1.70746000
Cl	2.60123900	-1.73822800	-1.07036800
O	-0.09261000	2.58443600	-2.10559300
H	2.08180100	1.32503300	-1.05551400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.4.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the B3LYP/aTZ level of theory

Table S76. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/aTZ level of theory.

N	-0.00006800	-1.26170700	1.36734900
N	-0.00006600	1.11472800	0.00000000
N	-0.00006800	-1.26170700	-1.36734900
P	-0.00001600	0.32962300	1.40005300
P	-0.00004400	-2.08292500	0.00000000
P	-0.00001600	0.32962300	-1.40005300
Cl	1.57599400	0.97544300	2.50324900
Cl	1.57615900	-3.36361900	0.00000000
Cl	-1.57588000	0.97553300	2.50338700
Cl	-1.57618100	-3.36368900	0.00000000
Cl	1.57599400	0.97544300	-2.50324900
Cl	-1.57588000	0.97553300	-2.50338700
Cl	-0.00004600	4.47482300	0.00000000
H	-0.00016300	3.17505400	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S77. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/aTZ level of theory.

N	-1.93333800	-0.13221600	0.00000000
N	0.44880900	1.20107700	0.00000000
N	0.45706400	-1.40303100	0.00000000
P	-1.20960100	1.25347800	0.00000000
P	-1.09543700	-1.51361500	0.00000000
P	1.48776600	-0.15561100	0.00000000
Cl	-1.75743800	2.40107400	1.57383600
Cl	-1.75306200	-2.61739900	1.57557300
Cl	-1.75743800	2.40107400	-1.57383600
Cl	-1.75306200	-2.61739900	-1.57557300
Cl	2.52135800	-0.58043800	1.70272800
Cl	2.52135800	-0.58043800	-1.70272800
Cl	3.06622300	1.98283800	0.00000000
H	1.00535500	2.06899300	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S78. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/aTZ level of theory.

N	-1.87311800	0.52775300	-0.00050700
N	0.81237400	1.05082300	-0.00017200
N	0.02441400	-1.39969000	0.00125200
P	-0.75134900	1.61197700	-0.00020200
P	-1.48164900	-1.04610400	0.00012600
P	1.43214400	-0.56797000	0.00034500
Cl	-0.90850100	2.88133300	1.57312200
Cl	-2.45820000	-1.89318500	1.57495100
Cl	-0.90810200	2.88165800	-1.57326300
Cl	-2.45652600	-1.89386900	-1.57543900
Cl	2.14750500	-1.39876600	1.75147600
Cl	2.14641900	-1.40017000	-1.75060400
Cl	3.48200800	0.67681100	-0.00078600
H	1.55766400	1.74309400	-0.00058100

Color code: P = orange, N = blue, Cl = green, H = white

Table S79. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/aTZ level of theory.

N	-1.96583500	-0.00481000	-0.03851700
N	0.43613800	1.26730400	-0.14287600
N	0.42941500	-1.29010500	-0.14229900
P	-1.20406400	1.36207000	-0.06590000
P	-1.12279700	-1.38223400	-0.05497400
P	1.56137200	-0.12842800	-0.02636600
Cl	-1.70315600	2.52237800	1.52800000
Cl	-1.70221000	-2.46300000	1.57059600
Cl	-1.80096200	2.53104600	-1.61506300
Cl	-1.84762800	-2.50919700	-1.58188900
Cl	2.12289100	-0.14816700	1.95498000
Cl	2.97046200	-1.41174100	-0.97056900
Cl	3.04001600	1.51051900	-0.60337600
H	0.92652000	2.14948300	-0.23349400

Color code: P = orange, N = blue, Cl = green, H = white

Table S80. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the B3LYP/aTZ level of theory.

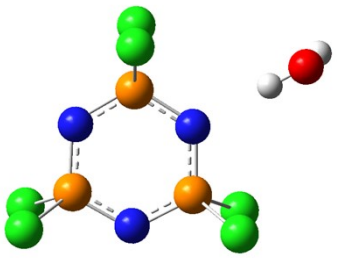
N	-1.75545400	0.70322800	-0.22271800
N	-0.14000100	-1.34333400	0.38214400
N	0.95839700	1.01440500	0.04604400
P	-1.63044300	-0.85077700	0.00325400
P	-0.47756600	1.65490900	-0.05591100
P	1.54391000	-0.47066600	0.08209600
Cl	-2.38808700	-1.82815200	-1.62133300
Cl	-0.50861300	2.96258700	-1.60374200
Cl	-2.88870800	-1.50564800	1.46484600
Cl	-0.76717300	2.87694500	1.54474700
Cl	1.73552400	-1.65216900	-1.63787600
Cl	3.57278600	0.22620400	-0.17905200
Cl	2.12301300	-1.43085000	1.85066900
H	-0.04061400	-2.32231100	0.61567700

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.5 Electronic structures fully optimized at the B3PW91/6-311+G(d,p) level of theory

Section 5.5.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the B3PW91/6-311+G(d,p) level of theory

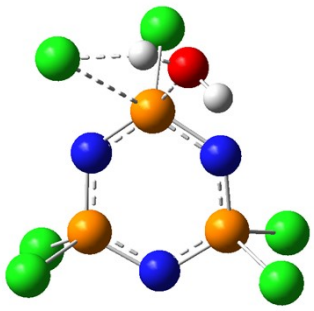
Table S81. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	0.60571900	-1.37087800	-0.01478000
P	0.50981600	1.43524200	0.00373900
P	-1.86031100	-0.05062900	0.01531000
N	1.32947400	0.05859300	-0.00941800
N	-0.98379800	-1.37991500	0.00240400
N	-1.07656300	1.33542000	0.02122100
Cl	1.30079300	-2.45923900	1.53336500
Cl	-3.11935900	-0.10452000	1.59461000
Cl	1.08928700	2.54623500	-1.58413200
Cl	1.13023600	2.54857800	1.56572200
Cl	-3.13434700	-0.08345400	-1.55400900
Cl	1.25979700	-2.41906800	-1.61624700
H	4.66685400	0.18042600	-0.64738200
O	4.33867500	0.16109800	0.25414600
H	3.37641600	0.12764600	0.16403500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

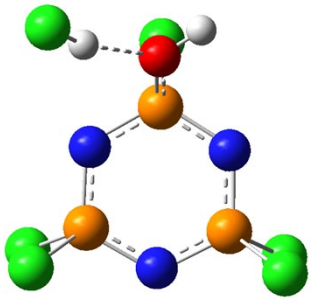
Table S82. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-1.17271200	-0.87160400	0.17122800
P	1.65131400	-0.70321700	-0.18695700
P	0.19115700	1.61753200	0.10311000
N	0.27598800	-1.50972700	-0.17641400
N	-1.05988200	0.69773300	0.45937700
N	1.58225100	0.88627900	-0.17791200
Cl	-2.01825700	-1.69859400	1.79010000
Cl	0.41029400	2.92643600	1.62067900
Cl	2.69786300	-1.29511700	-1.81395800
Cl	2.83166100	-1.34569900	1.33383900
Cl	-0.22483600	2.82214900	-1.46876600
Cl	-3.50490200	-0.18682400	-0.94220200
H	-2.70998600	-1.71200700	-1.35571000
O	-1.87391200	-2.21974600	-0.98658500
H	-1.19456200	-2.47065000	-1.63245600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

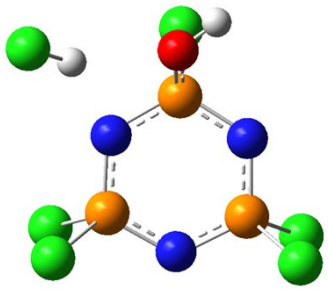
Table S83. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-0.68629700	-1.09830100	0.65422500
P	1.74365500	-0.55158800	-0.59142200
P	0.07294200	1.53954300	0.22518600
N	0.64053700	-1.58442700	-0.08717100
N	-0.99553300	0.45813300	0.70145700
N	1.43300000	0.99800900	-0.40377100
Cl	-0.69082100	-1.87184300	2.53386100
Cl	0.52063700	2.77196700	1.76616500
Cl	2.13479500	-0.92690100	-2.54159100
Cl	3.52129400	-0.96811800	0.28321900
Cl	-0.81929100	2.79309100	-1.08343400
Cl	-4.84912000	-0.59550000	-1.24397100
H	-3.70624900	-0.86428000	-0.70623300
O	-1.97465900	-1.78607000	-0.01096800
H	-1.89441400	-2.73981200	-0.14173100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

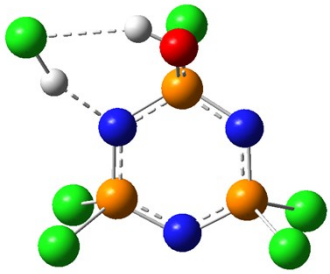
Table S84. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-0.49249100	-1.39166600	0.28515000
P	1.87961200	-0.18489100	-0.53278500
P	-0.24286400	1.37447700	0.41289700
N	0.96423200	-1.47660500	-0.35967400
N	-1.12213900	0.04952700	0.52696100
N	1.25389000	1.21631400	-0.10953500
Cl	-0.48473900	-2.46332300	2.01538000
Cl	-0.20270300	2.32521000	2.19920100
Cl	2.50398900	-0.08939500	-2.45631700
Cl	3.62297100	-0.44162300	0.46357300
Cl	-1.23025800	2.69313300	-0.75453700
Cl	-4.64974400	-0.51564000	-1.25173500
H	-3.46285500	-0.77019500	-0.82036500
O	-1.56776100	-2.16181900	-0.61050600
H	-1.34256600	-3.07086300	-0.84337300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

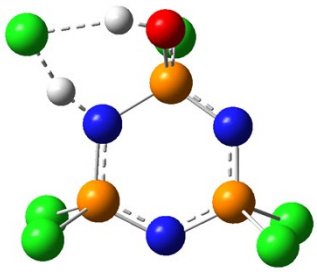
Table S85. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-0.56302600	-1.40848000	-0.14208000
P	1.94009100	-0.19151300	-0.25316100
P	-0.32755900	1.36756600	0.26268500
N	0.99647900	-1.45634900	-0.42565500
N	-1.22453800	0.06273200	0.01348600
N	1.24299700	1.19516300	0.11744900
Cl	-0.98148000	-2.46231300	1.54392000
Cl	-0.73721800	2.15377400	2.08307800
Cl	3.03247300	0.04231000	-1.93689800
Cl	3.36133200	-0.57683500	1.13283900
Cl	-0.98804900	2.81462800	-0.98288900
Cl	-4.10679000	-0.52951200	-0.89157700
H	-2.97766900	-0.02162800	-0.41414000
O	-1.30786900	-2.19643500	-1.29257100
H	-2.27110000	-2.04618900	-1.31793300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

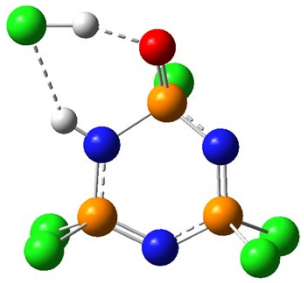
Table S86. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-0.52671500	-1.49689300	-0.15080800
P	1.89619900	-0.10884900	-0.29127200
P	-0.43137600	1.35013200	0.33600300
N	1.00393500	-1.39502200	-0.53587600
N	-1.25913900	-0.01507300	0.02742500
N	1.13330800	1.20478800	0.20732100
Cl	-0.71210800	-2.48693200	1.60329800
Cl	-0.89587000	2.04386700	2.16857800
Cl	2.91768100	0.30679500	-1.97819500
Cl	3.36570500	-0.50389600	1.03387200
Cl	-1.17025000	2.76442000	-0.88432200
Cl	-3.76823000	-0.62542200	-1.06928300
H	-2.41480700	-0.07922000	-0.35707500
O	-1.37627500	-2.27932700	-1.18970200
H	-2.32112900	-1.89500300	-1.28334600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S87. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the B3PW91/6-311+G(d,p) level of theory.



P	-0.68293200	-1.48173100	-0.13996200
P	1.88001400	-0.31322300	-0.36433100
P	-0.21644200	1.45293200	0.29192500
N	0.82572800	-1.43967500	-0.65948400
N	-1.20001900	0.17358800	-0.00488400
N	1.29812300	1.08546300	0.17937200
Cl	-0.64497200	-2.10886300	1.81238700
Cl	-0.61671900	2.24142300	2.10215600
Cl	2.95731000	0.03774800	-2.03208600
Cl	3.29060800	-0.89930800	0.95959500
Cl	-0.78869900	2.92332300	-0.96297600
Cl	-4.31133400	-0.70073500	-1.00075300
H	-2.20962700	0.31157300	-0.09028800
O	-1.71688900	-2.21966000	-0.89963600
H	-3.29699300	-1.55057100	-1.06360900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.5.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the B3PW91/6-311+G(d,p) level of theory

Table S88. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the B3PW91/6-311+G(d,p) level of theory.

P	0.03129200	1.68236600	-0.57857700
P	-1.41679900	-0.60319300	0.05631800
P	1.37390900	-0.67803500	0.05314800
N	-1.34909300	0.91102900	-0.41971500
N	1.37912700	0.83277400	-0.44145800
N	-0.03973800	-1.36681100	0.30278200
Cl	0.11496800	3.21672200	0.76183000
Cl	2.48625100	-0.85846000	1.73935400
Cl	-2.52902700	-1.65324400	-1.27112100
Cl	-2.53480900	-0.73619100	1.74052100
Cl	2.43688600	-1.79314500	-1.26427700
O	-0.01494400	2.43192600	-1.98250400
H	0.79890000	2.90200000	-2.20179500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S89. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the B3PW91/6-311+G(d,p) of theory.

P	-0.16577500	1.73303400	-0.67046000
P	-1.37592300	-0.69081100	0.03901200
P	1.43411100	-0.54878200	0.16321600
N	-1.42863700	0.77378200	-0.56094900
N	1.32089500	0.95606700	-0.41795400
N	0.05320400	-1.24617700	0.49488900
Cl	-0.41835800	3.24398600	0.64283500
Cl	2.58085400	-0.59988500	1.82440400
Cl	-2.20592000	-1.97537000	-1.28451600
Cl	-2.61270500	-0.84786100	1.62875800
Cl	2.53002700	-1.61715400	-1.15965200
O	0.34635500	2.27442200	-2.01231200
H	1.36845200	1.55412700	-1.57101300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S90. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the B3PW91/6-311+G(d,p) level of theory.

P	-0.21816800	1.74240200	-0.93857400
P	-1.38337900	-0.65570100	0.02887900
P	1.42906100	-0.56639800	0.10379900
N	-1.39288600	0.65805600	-0.82473900
N	1.26513400	0.82354000	-0.75063900
N	0.05859500	-1.18875700	0.51555400
Cl	-0.25150000	2.84027400	0.80810200
Cl	2.58946300	-0.26469200	1.72805000
Cl	-2.28958500	-2.13120600	-1.00770600
Cl	-2.52686500	-0.52450500	1.69394500
Cl	2.57341600	-1.80251500	-1.01311800
O	-0.07856200	2.60966800	-2.11364900
H	2.08611300	1.27321000	-1.14122900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.5.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the B3PW91/6-311+G(d,p) level of theory

Table S91. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.

N	0.00013100	-1.24379500	1.35740300
N	0.00013100	1.11675700	0.00000000
N	0.00013100	-1.24379500	-1.35740300
P	0.00013100	0.34365600	1.40742500
P	0.00004600	-2.07632200	0.00000000
P	0.00013100	0.34365600	-1.40742500
Cl	1.57502500	0.98415600	2.49390400
Cl	1.57454000	-3.34160200	0.00000000
Cl	-1.57475600	0.98417700	2.49390400
Cl	-1.57469000	-3.34131500	0.00000000
Cl	1.57502500	0.98415600	-2.49390400
Cl	-1.57475600	0.98417700	-2.49390400
Cl	-0.00079800	4.35690300	0.00000000
H	-0.00039900	3.04986800	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S92. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.

N	-1.92188100	-0.14186800	0.00000000
N	0.44869700	1.18918300	0.00000000
N	0.44803100	-1.40088500	0.00000000
P	-1.21063400	1.24747500	0.00000000
P	-1.10093500	-1.53046200	0.00000000
P	1.48334400	-0.16666600	0.00000000
Cl	-1.75004800	2.38253600	1.57266200
Cl	-1.75004800	-2.61961400	1.57430400
Cl	-1.75004800	2.38253600	-1.57266200
Cl	-1.75004800	-2.61961400	-1.57430400
Cl	2.53243800	-0.57481100	1.68111100
Cl	2.53243800	-0.57481100	-1.68111100
Cl	3.02760200	2.04521800	0.00000000
H	1.03057000	2.05530500	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S93. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.

N	-1.88062800	0.46444700	0.16367400
N	0.77782100	1.08795000	0.07858100
N	0.06110800	-1.31753100	-0.31960600
P	-0.80965400	1.59103900	0.07036100
P	-1.43689000	-1.08520000	-0.02797600
P	1.45997500	-0.50171500	-0.08862300
Cl	-0.96023600	2.90843500	1.58632800
Cl	-2.12917600	-2.07186300	1.60880200
Cl	-1.04867000	2.77239500	-1.55494500
Cl	-2.57483900	-1.86745200	-1.50274600
Cl	2.04359000	-1.55381700	1.58903200
Cl	2.28258600	-1.13972000	-1.86156800
Cl	3.42214500	0.74520400	0.19648200
H	1.48863300	1.80998600	0.19150300

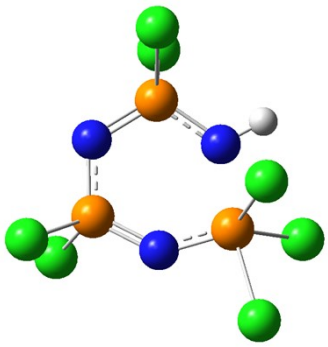
Color code: P = orange, N = blue, Cl = green, H = white

Table S94. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.

N	-1.95718600	0.00048700	-0.03400100
N	0.44343900	1.26374700	-0.16422400
N	0.41738600	-1.27222500	-0.12620400
P	-1.19883000	1.36442600	-0.06787300
P	-1.12687100	-1.38485100	-0.04552100
P	1.56639800	-0.12995900	-0.02912200
Cl	-1.66919400	2.51761300	1.52822200
Cl	-1.71350100	-2.44871200	1.57547100
Cl	-1.79226900	2.52715100	-1.61100500
Cl	-1.84573100	-2.49588000	-1.57423500
Cl	2.12371300	-0.17263200	1.94416100
Cl	2.92427100	-1.41575600	-1.00968900
Cl	3.03924300	1.49776100	-0.57802000
H	0.93303600	2.14943500	-0.26462600

Color code: P = orange, N = blue, Cl = green, H = white

Table S95. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the B3PW91/6-311+G(d,p) level of theory.



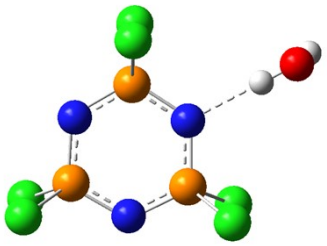
N	-1.75475400	0.65921600	-0.26219800
N	-0.11453600	-1.32799700	0.41741200
N	0.92893700	1.03023700	0.03056500
P	-1.60927200	-0.88494100	0.00174700
P	-0.51359400	1.64837500	-0.06949900
P	1.56694000	-0.42595300	0.08825000
Cl	-2.31244300	-1.89940100	-1.61287300
Cl	-0.56545400	2.96408100	-1.59456200
Cl	-2.86850400	-1.52795400	1.45640500
Cl	-0.83680500	2.82422300	1.54774300
Cl	1.75578200	-1.64422100	-1.59278000
Cl	3.55182100	0.33186100	-0.19372100
Cl	2.15318200	-1.36000400	1.85473600
H	0.00254300	-2.29837800	0.68794900

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.6 Electronic structures fully optimized at the *ω*B97X-D/6-311+G(d,p) level of theory

Section 5.6.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the *ω*B97X-D /6-311+G(d,p) level of theory

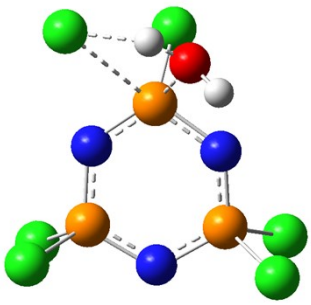
Table S96. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	0.61846300	-1.36673600	-0.01125700
P	0.51982100	1.43545800	0.00747400
P	-1.84399100	-0.05062600	0.01298700
N	1.32763100	0.06101400	-0.00479500
N	-0.96396300	-1.36947800	0.00242200
N	-1.05889600	1.32699300	0.02156800
Cl	1.31228400	-2.44394700	1.53614400
Cl	-3.09951800	-0.10557700	1.58598800
Cl	1.10292700	2.53711100	-1.57616100
Cl	1.13817200	2.53828500	1.56874400
Cl	-3.10384300	-0.08372000	-1.55872400
Cl	1.27745600	-2.40416300	-1.60843600
H	4.59550600	0.16918600	-0.66349000
O	4.28623000	0.15505600	0.24233300
H	3.32440800	0.12667700	0.17378900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

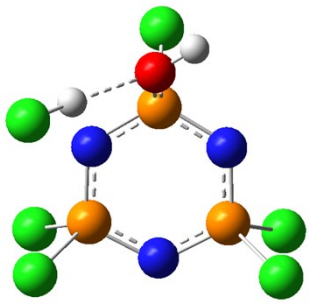
Table S97. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	-1.21087000	-0.82756200	0.07428000
P	1.63347300	-0.72977900	-0.14746500
P	0.22547000	1.61965600	0.10011300
N	0.24353000	-1.47844600	-0.21882800
N	-1.07519900	0.73567800	0.30507500
N	1.60428900	0.85425900	-0.07825600
Cl	-1.99847800	-1.73734400	1.67457100
Cl	0.35396400	2.88282200	1.65750900
Cl	2.73030600	-1.29212400	-1.74799900
Cl	2.73219600	-1.44282100	1.39345100
Cl	-0.03539200	2.86156800	-1.46903300
Cl	-3.58252700	-0.18592800	-0.76204400
H	-2.69848500	-1.60998400	-1.55406100
O	-1.83605100	-2.03453700	-1.21896000
H	-1.14370200	-2.29377800	-1.84383100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

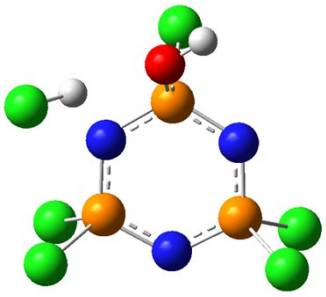
Table S98. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	-0.39072000	-1.45979600	0.38286100
P	1.78899100	-0.04539200	-0.60387100
P	-0.38198200	1.31386700	0.51366900
N	1.01066100	-1.40693900	-0.36293100
N	-1.09396700	-0.08715700	0.73046400
N	1.06503100	1.28368500	-0.13721500
Cl	-0.18555300	-2.58386000	2.05341500
Cl	-0.27798500	2.29381500	2.27265400
Cl	2.25502600	0.09518900	-2.56149100
Cl	3.60724500	-0.13945100	0.26554000
Cl	-1.58816900	2.49374800	-0.58016200
Cl	-4.17372100	-0.57781700	-1.47274200
H	-3.14177300	-1.15875200	-0.96282900
O	-1.45645100	-2.28266500	-0.47794700
H	-1.14938400	-3.12485100	-0.82835800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S99. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	-0.36832500	-1.48727400	0.30415900
P	1.81019600	-0.00457300	-0.57910700
P	-0.41059900	1.28051900	0.52844500
N	1.04972900	-1.38589300	-0.40394000
N	-1.11104700	-0.13693500	0.66250800
N	1.05426200	1.29525200	-0.08148900
Cl	-0.17628700	-2.64208700	1.95624500
Cl	-0.36768600	2.18524700	2.33018600
Cl	2.31634000	0.21361100	-2.51974000
Cl	3.61025400	-0.10018300	0.32677700
Cl	-1.60163600	2.49200400	-0.54674500
Cl	-4.19370900	-0.53456700	-1.45049300
H	-3.13865600	-1.07665500	-0.94781000
O	-1.39887600	-2.30765100	-0.59641200
H	-1.07369500	-3.13762000	-0.95881800

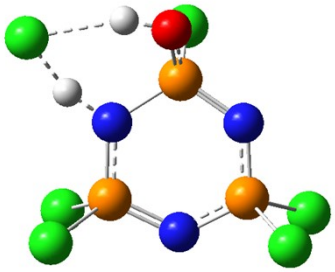
Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S100. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

P	-0.55701200	-1.40023800	-0.16347600
P	1.94720000	-0.19234300	-0.24802000
P	-0.31668500	1.36654300	0.24588800
N	0.99964400	-1.44544600	-0.42626100
N	-1.20407900	0.06445000	0.00846600
N	1.24601200	1.19236200	0.09000600
Cl	-1.00128700	-2.46360700	1.50238300
Cl	-0.71953500	2.14484100	2.06399800
Cl	3.07148500	0.02245500	-1.90388500
Cl	3.32563100	-0.57528800	1.17305200
Cl	-0.98238700	2.80514200	-0.99622700
Cl	-4.15401200	-0.51179300	-0.83186300
H	-3.02908200	-0.00068300	-0.37921500
O	-1.28659500	-2.17411700	-1.32767300
H	-2.24996200	-2.06510400	-1.34755300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

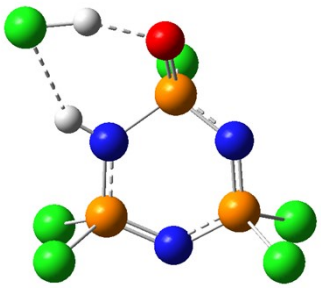
Table S101. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	-0.51628400	-1.49224800	-0.17783600
P	1.90436100	-0.10333100	-0.27806600
P	-0.42860500	1.34933700	0.32283400
N	1.01355100	-1.38186500	-0.52850300
N	-1.24256400	-0.01823100	0.01614600
N	1.12857600	1.20371600	0.19330600
Cl	-0.74213200	-2.50143800	1.55149500
Cl	-0.90400000	2.02511600	2.15076400
Cl	2.95249800	0.30507000	-1.94098100
Cl	3.33559700	-0.49912900	1.07799100
Cl	-1.16967300	2.75091300	-0.89737600
Cl	-3.78440700	-0.60158600	-1.00910800
H	-2.39504800	-0.07501000	-0.32959300
O	-1.33802500	-2.25936200	-1.24646600
H	-2.28378100	-1.92390700	-1.32665900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S102. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



P	-0.66357700	-1.48643100	-0.15962400
P	1.88491400	-0.29343700	-0.36713800
P	-0.22923700	1.43984000	0.29031300
N	0.84214100	-1.41965700	-0.66626100
N	-1.19503700	0.15632700	-0.01878000
N	1.28231800	1.09316100	0.16518300
Cl	-0.61893100	-2.10165700	1.79215000
Cl	-0.64122600	2.18638100	2.10816000
Cl	2.97153500	0.06990300	-2.01783100
Cl	3.27611200	-0.87186100	0.97088200
Cl	-0.82108400	2.91160200	-0.94115200
Cl	-4.30685000	-0.69658000	-0.99064700
H	-2.20438600	0.28686300	-0.09330100
O	-1.68421800	-2.23648000	-0.91295400
H	-3.32180300	-1.56581400	-1.08389000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.6.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the *ω*B97X-D/6-311+G(d,p) level of theory

Table S103. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

P	0.03341800	1.67291900	-0.60433200
P	-1.41634300	-0.60028800	0.05082600
P	1.37153900	-0.67753700	0.05104400
N	-1.33783400	0.89667000	-0.45524100
N	1.37017900	0.81675000	-0.47301200
N	-0.04111100	-1.35162100	0.30121000
Cl	0.11038000	3.17590500	0.76048600
Cl	2.46354600	-0.81391800	1.74581300
Cl	-2.53099300	-1.67040000	-1.24500600
Cl	-2.51574300	-0.69054900	1.74183700
Cl	2.43717900	-1.81365000	-1.23217700
O	0.00031200	2.43810400	-1.99310700
H	0.83539300	2.85055400	-2.23513100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S104. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the ωB97X-D/6-311+G(d,p) of theory.

P	-0.15242600	1.72077700	-0.69029200
P	-1.37654600	-0.68268000	0.03822900
P	1.42695800	-0.55154000	0.16959700
N	-1.40899500	0.76284300	-0.59052300
N	1.31840900	0.94157900	-0.42314700
N	0.04525300	-1.22922500	0.50356100
Cl	-0.40642300	3.21736500	0.63158200
Cl	2.57076900	-0.58247800	1.82311900
Cl	-2.20233900	-1.98646200	-1.25745500
Cl	-2.61317500	-0.79115500	1.62382600
Cl	2.50534700	-1.63799200	-1.14163700
O	0.36829200	2.26308000	-2.02090800
H	1.38018300	1.54289600	-1.57536700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S105. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

P	-0.18585000	1.72968500	-0.95072200
P	-1.39364500	-0.63416900	0.02745500
P	1.41381300	-0.58782700	0.10215600
N	-1.37248900	0.66881800	-0.83034100
N	1.27413500	0.78976600	-0.76812300
N	0.03708800	-1.18449100	0.50570900
Cl	-0.19159100	2.81061200	0.80110900
Cl	2.56045400	-0.26700600	1.72311100
Cl	-2.32681700	-2.09726200	-0.98881900
Cl	-2.52129900	-0.45676700	1.69039200
Cl	2.54398500	-1.84656000	-0.98771800
O	-0.03587600	2.60165300	-2.11468900
H	2.10065900	1.22149700	-1.16385000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

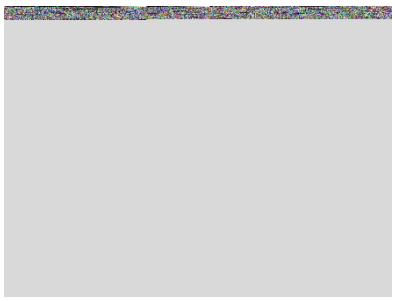
Section 5.6.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the *ω*B97X-D/6-311+G(d,p) level of theory

Table S106. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

N	-0.00009900	1.23827400	1.34840100
N	-0.00007900	-1.10146400	0.00000000
N	-0.00009900	1.23827400	-1.34840100
P	-0.00009900	-0.34199300	1.40489400
P	-0.00005100	2.07295300	0.00000000
P	-0.00009900	-0.34199300	-1.40489400
Cl	-1.57230600	-0.98530400	2.48104700
Cl	-1.57267700	3.32953100	0.00000000
Cl	1.57207800	-0.98532100	2.48107900
Cl	1.57271500	3.32936200	0.00000000
Cl	-1.57230600	-0.98530400	-2.48104700
Cl	1.57207800	-0.98532100	-2.48107900
Cl	0.00073100	-4.33131800	0.00000000
H	0.00036700	-3.02763600	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S107. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.



N	-1.74061700	0.80015100	0.00006000
N	0.96317600	0.82645300	0.00006100
N	-0.28199300	-1.42680500	0.00019900
P	-0.45761700	1.67532100	0.00022900
P	-1.69923600	-0.80585600	-0.00001800
P	1.21780900	-0.85389400	-0.00003900
Cl	-0.37726600	2.91961000	1.57053500
Cl	-2.78498000	-1.44326400	1.57211700
Cl	-0.37723100	2.92018200	-1.56961100
Cl	-2.78452400	-1.44306400	-1.57257000
Cl	1.92211200	-1.70834800	1.68428500
Cl	1.92159500	-1.70817300	-1.68468000
Cl	3.63500100	0.28934400	-0.00035700
H	1.87167700	1.32097000	-0.00004100

Color code: P = orange, N = blue, Cl = green, H = white

Table S108. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

N	1.85863700	0.46161900	-0.26226400
N	-0.78477600	1.08671000	-0.12603900
N	-0.04865800	-1.27641700	0.37862600
P	0.79911100	1.58505400	-0.11500200
P	1.43312100	-1.07261500	0.02087700
P	-1.45398800	-0.49012800	0.10793600
Cl	0.92954200	2.94225200	-1.58341000
Cl	2.05708500	-2.13057000	-1.58849600
Cl	1.05120300	2.69745000	1.54872400
Cl	2.61641700	-1.78250800	1.48763500
Cl	-1.99936000	-1.61225300	-1.52955900
Cl	-2.25776200	-1.04396400	1.90918700
Cl	-3.41851000	0.69155600	-0.23669100
H	-1.48651100	1.80859700	-0.26504500

Color code: P = orange, N = blue, Cl = green, H = white

Table S109. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

N	-1.94452000	0.01096200	-0.03307200
N	0.44899100	1.25635900	-0.22745200
N	0.40398000	-1.26039500	-0.18603700
P	-1.18503900	1.36577100	-0.07933700
P	-1.12980700	-1.37594400	-0.05476900
P	1.55752600	-0.13283000	-0.05846000
Cl	-1.58455200	2.49983600	1.54004200
Cl	-1.66526500	-2.40812800	1.59662900
Cl	-1.81013000	2.54110000	-1.58842800
Cl	-1.89258300	-2.49708500	-1.54325800
Cl	2.04423800	-0.17056200	1.92858100
Cl	2.92155900	-1.43026100	-0.99335600
Cl	3.04957200	1.46236300	-0.56734400
H	0.93239200	2.14307600	-0.32431600

Color code: P = orange, N = blue, Cl = green, H = white

Table S110. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the ωB97X-D/6-311+G(d,p) level of theory.

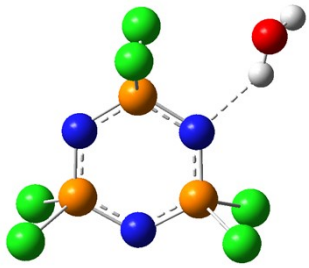
N	-1.73763300	0.64762500	-0.27812100
N	-0.10906600	-1.32696000	0.42525200
N	0.91443500	1.02485500	0.07008000
P	-1.59686000	-0.88739300	-0.00419700
P	-0.51451800	1.64558400	-0.06584900
P	1.55582100	-0.42395100	0.10277400
Cl	-2.26680500	-1.91623000	-1.61229800
Cl	-0.54121900	2.95045500	-1.59281700
Cl	-2.85879900	-1.52077700	1.44046900
Cl	-0.87818300	2.81342000	1.53909300
Cl	1.73023900	-1.59883100	-1.60096300
Cl	3.53314200	0.33427800	-0.18351500
Cl	2.15551600	-1.36460600	1.85009800
H	0.00306200	-2.29329100	0.70744000

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.7 Electronic structures fully optimized at the M06-2X/6-311+G(d,p) level of theory

Section 5.7.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the M06-2X/6-311+G(d,p) level of theory

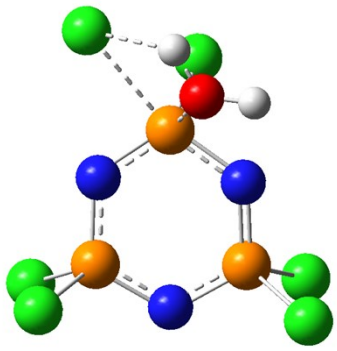
Table S111. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	0.49804000	-1.54725600	-0.03798300
P	0.67593400	1.25292800	0.05438300
P	-1.82445400	-0.00436600	0.01944200
N	1.34510200	-0.19915400	-0.01172100
N	-1.08105400	-1.40897800	-0.02593400
N	-0.91136400	1.29059700	0.07806500
Cl	1.07952900	-2.71546300	1.49541400
Cl	-3.09990400	0.01300400	1.57580500
Cl	1.33807300	2.34016500	-1.50313300
Cl	1.38967000	2.24433200	1.64057700
Cl	-3.06802100	0.12953700	-1.56002800
Cl	1.06175600	-2.63248800	-1.64044700
H	4.59612300	0.78159000	-0.60973100
O	4.06121100	0.82284800	0.18505000
H	3.37204700	0.15823700	0.06882300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

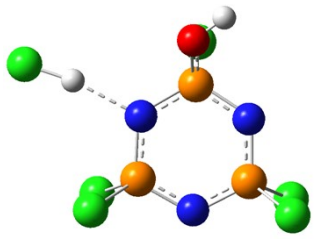
Table S112. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS***) for the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	-1.27362700	-0.72850500	-0.08767600
P	1.58437400	-0.79549200	-0.09953400
P	0.28145300	1.62433500	0.11364400
N	0.17271500	-1.45454500	-0.32170800
N	-1.10392600	0.83553300	0.08022600
N	1.62703900	0.78415900	0.09260200
Cl	-1.95510800	-1.79790300	1.49433700
Cl	0.27335600	2.81757400	1.73007700
Cl	2.78786800	-1.30605100	-1.64179800
Cl	2.54278900	-1.65061400	1.46448400
Cl	0.29660000	2.94678900	-1.40954800
Cl	-3.68074100	-0.23012700	-0.52547200
H	-2.78338700	-1.46897400	-1.71462300
O	-1.77736100	-1.51796600	-1.64521700
H	-1.25247100	-2.30277200	-1.88334800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S113. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB***) for the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	0.16009700	1.51987400	-0.56118300
P	-2.01082900	-0.14711400	-0.06190500
P	0.59069000	-1.15466600	0.11023300
N	-1.40287300	1.22606800	-0.57547600
N	1.12388400	0.25902900	-0.40881600
N	-0.98185100	-1.32305800	0.22573800
Cl	0.55475700	2.83942600	0.93014400
Cl	1.43837400	-1.56191800	1.89083300
Cl	-3.39040100	-0.77745900	-1.38075700
Cl	-3.11398100	0.16757300	1.59856800
Cl	1.34985800	-2.58394200	-1.07486400
Cl	4.33826900	0.38427400	-0.16083600
H	3.05327300	0.43973700	-0.34847800
O	0.61681500	2.28675500	-1.86519500
H	0.11935200	3.08855400	-2.06870700

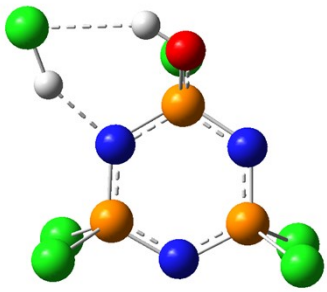
Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S114. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

P	-0.52977200	-1.33588800	-0.45731900
P	1.98654400	-0.20825100	-0.11865100
P	-0.28374600	1.38399900	0.13299200
N	1.05524800	-1.41405800	-0.57763600
N	-1.16448500	0.13059000	-0.32703200
N	1.29399000	1.19559900	0.18757700
Cl	-1.13294800	-2.46873700	1.12127100
Cl	-0.93259300	2.02127300	1.93262600
Cl	3.41065500	0.05532100	-1.51083600
Cl	3.05698000	-0.75445900	1.50306000
Cl	-0.73974200	2.92871200	-1.06652000
Cl	-4.32890400	-0.47144200	-0.38586600
H	-3.11198400	-0.01222700	-0.38463400
O	-1.23329900	-2.04006200	-1.68766400
H	-1.57891200	-2.93143300	-1.54324800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

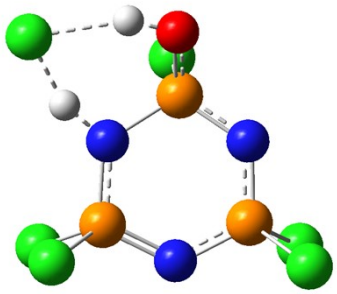
Table S115. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	-0.60505900	-1.34907700	-0.23693600
P	1.94239900	-0.24671800	-0.24163000
P	-0.27177400	1.40113100	0.17976200
N	0.95072800	-1.45370700	-0.50560600
N	-1.20578500	0.14244100	-0.11674100
N	1.28982700	1.17661500	0.04319300
Cl	-1.07564400	-2.32279700	1.47927200
Cl	-0.67857400	2.12999500	2.01881300
Cl	3.20828400	-0.09214300	-1.79297000
Cl	3.17864100	-0.70055700	1.28771900
Cl	-0.85772900	2.90772100	-1.01511700
Cl	-4.18102700	-0.56540300	-0.73436800
H	-3.07871900	0.05436300	-0.39009500
O	-1.36411000	-2.14948600	-1.35856600
H	-2.33244800	-2.06182000	-1.34216300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

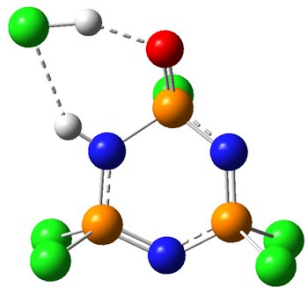
Table S116. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	-0.52004800	-1.48385900	-0.20851200
P	1.89684300	-0.10545200	-0.29904100
P	-0.43279200	1.35824800	0.30688100
N	0.99622100	-1.36376900	-0.62478100
N	-1.24986400	-0.00317800	-0.03048100
N	1.12632100	1.20565600	0.18267300
Cl	-0.65807200	-2.41474700	1.57506500
Cl	-0.91399900	2.00271300	2.14277600
Cl	3.01324500	0.32913200	-1.90485600
Cl	3.26941000	-0.55814800	1.09949400
Cl	-1.16848300	2.78141500	-0.88782900
Cl	-3.80376100	-0.67525300	-0.99175700
H	-2.39150600	-0.06764700	-0.34208700
O	-1.38575200	-2.28815800	-1.20333800
H	-2.34303000	-1.93901100	-1.27217700

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S117. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the M06-2X/6-311+G(d,p) level of theory.



P	-0.65932300	-1.47287600	-0.21587800
P	1.88869600	-0.30282100	-0.35448100
P	-0.23621600	1.44086400	0.25192400
N	0.84771700	-1.41377400	-0.72897600
N	-1.19848900	0.17459800	-0.13643800
N	1.27980100	1.08883100	0.16637600
Cl	-0.59706600	-1.98398400	1.76890100
Cl	-0.70730400	2.12851700	2.07800300
Cl	3.06575300	0.06569700	-1.93668300
Cl	3.19949700	-0.91879200	1.04545900
Cl	-0.77670500	2.95806300	-0.94399300
Cl	-4.32534300	-0.74892900	-0.93265800
H	-2.20996300	0.30360400	-0.21217900
O	-1.67734000	-2.26256900	-0.92507800
H	-3.37202800	-1.63788100	-1.06089300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.7.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the M06-2X/6-311+G(d,p) level of theory

Table S118. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the M06-2X/6-311+G(d,p) level of theory.

P	0.03044600	1.65608900	-0.65833900
P	-1.41632100	-0.60147500	0.03409100
P	1.37344300	-0.67422400	0.03636000
N	-1.34294400	0.87215000	-0.54552200
N	1.37124600	0.79696400	-0.55765900
N	-0.03922800	-1.35344100	0.29210000
Cl	0.09973000	3.09851900	0.77322400
Cl	2.43322900	-0.72152400	1.75626700
Cl	-2.56474100	-1.71986200	-1.18232800
Cl	-2.47902300	-0.60586200	1.75092800
Cl	2.47338600	-1.85454200	-1.16872300
O	0.00651700	2.48018500	-2.00874200
H	0.84694100	2.89857000	-2.23344000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S119. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the M06-2X/6-311+G(d,p) of theory.

P	-0.19985600	1.70728500	-0.72675600
P	-1.35128900	-0.71653500	0.03212000
P	1.44622800	-0.50004800	0.18182900
N	-1.41684100	0.69159600	-0.68060800
N	1.29819800	0.98211400	-0.43317100
N	0.07984300	-1.19954500	0.54762900
Cl	-0.53968500	3.15417900	0.63148200
Cl	2.61025500	-0.48197700	1.81746000
Cl	-2.12296300	-2.10705000	-1.20113100
Cl	-2.60435100	-0.77959400	1.60569900
Cl	2.53026900	-1.59075700	-1.12123100
O	0.32849200	2.30065400	-2.02794100
H	1.36747100	1.60345800	-1.57005200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S120. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the M06-2X/6-311+G(d,p) level of theory.

P	-0.17884600	1.71017200	-0.98421900
P	-1.39956600	-0.61964100	0.01577000
P	1.41177800	-0.58903700	0.09071900
N	-1.37283400	0.65076800	-0.89684300
N	1.27672600	0.75268700	-0.83701400
N	0.02952400	-1.17536700	0.50150900
Cl	-0.16469700	2.70848800	0.81812700
Cl	2.53769900	-0.20083200	1.71029600
Cl	-2.36536400	-2.10375900	-0.93067700
Cl	-2.50461500	-0.36234300	1.68235700
Cl	2.55895400	-1.88334200	-0.93257700
O	-0.02443000	2.62619000	-2.11023500
H	2.10744200	1.18185700	-1.23366400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.7.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the M06-2X/6-311+G(d,p) level of theory

Table S121. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

N	0.00046500	1.24130800	1.35329100
N	-0.00049300	-1.10276500	-0.00000200
N	0.00046400	1.24131000	-1.35329200
P	-0.00011200	-0.34196400	1.40636500
P	0.00082700	2.07393200	0.00000000
P	-0.00011300	-0.34196200	-1.40636700
Cl	-1.56908500	-0.98884000	2.48222600
Cl	-1.56821800	3.33195900	0.00000200
Cl	1.56855600	-0.98999400	2.48199600
Cl	1.57097400	3.33058600	0.00000000
Cl	-1.56908700	-0.98883700	-2.48222800
Cl	1.56855400	-0.98999100	-2.48200100
Cl	-0.00086500	-4.32215900	0.00000700
H	-0.00081500	-3.02164900	0.00000200

Color code: P = orange, N = blue, Cl = green, H = white

Table S122. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

N	-1.71893600	0.80544900	-0.31275300
N	0.98073700	0.80743600	-0.09911100
N	-0.33475200	-1.34443200	0.47020300
P	-0.43392400	1.66939000	-0.12251600
P	-1.70851200	-0.77208700	0.00602100
P	1.16922400	-0.85304300	0.18078400
Cl	-0.49186500	2.78243100	1.55091000
Cl	-3.09893100	-1.15903700	1.39717200
Cl	-0.21123800	3.01833000	-1.57173400
Cl	-2.43618400	-1.70055900	-1.62936600
Cl	2.06951700	-1.44004000	1.86757100
Cl	1.70191400	-1.96017100	-1.41115100
Cl	3.65505600	0.23541900	-0.26953300
H	1.90825400	1.25858300	-0.24847700

Color code: P = orange, N = blue, Cl = green, H = white

Table S123. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

N	1.85781700	0.38782300	-0.46100600
N	-0.76054100	1.12433900	-0.23883800
N	-0.06179900	-1.16594700	0.54679100
P	0.84886500	1.54647900	-0.20217300
P	1.38634900	-1.09154000	0.01296400
P	-1.46538900	-0.40761600	0.15189400
Cl	1.01837300	2.99390900	-1.56672600
Cl	1.79831600	-2.31870100	-1.54198000
Cl	1.16876800	2.50814300	1.54385600
Cl	2.66327300	-1.73808700	1.42519400
Cl	-1.97557000	-1.70734000	-1.36214000
Cl	-2.29836000	-0.75649400	1.98666500
Cl	-3.39666400	0.72473400	-0.36163100
H	-1.42400100	1.86186500	-0.46397000

Color code: P = orange, N = blue, Cl = green, H = white

Table S124. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

N	-1.94802900	-0.00357100	-0.05898900
N	0.43980800	1.26637000	-0.28300800
N	0.41243400	-1.25558000	-0.31612800
P	-1.19425800	1.35777800	-0.09776700
P	-1.11252600	-1.38197100	-0.08212800
P	1.55423800	-0.12071900	-0.10457900
Cl	-1.55797200	2.45844200	1.55287900
Cl	-1.53987900	-2.35763500	1.63675500
Cl	-1.86321700	2.55939400	-1.56285900
Cl	-1.94279200	-2.56473300	-1.47617200
Cl	1.94963600	-0.22431000	1.90061500
Cl	2.95635200	-1.36883400	-1.03750300
Cl	3.05956700	1.49517700	-0.47150100
H	0.90987600	2.16562600	-0.34367100

Color code: P = orange, N = blue, Cl = green, H = white

Table S125. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the M06-2X/6-311+G(d,p) level of theory.

N	-1.71464200	0.58069500	-0.43684900
N	-0.08455800	-1.26738400	0.54995200
N	0.90434600	1.07627900	0.06001500
P	-1.55301000	-0.92580400	-0.02434400
P	-0.55364900	1.62932000	-0.11352800
P	1.56411800	-0.36733900	0.13405000
Cl	-2.08208400	-2.09298600	-1.58534300
Cl	-0.58377600	3.00110100	-1.57320000
Cl	-2.88606700	-1.49310000	1.38143400
Cl	-1.04904000	2.70090600	1.52652900
Cl	1.69767900	-1.60355900	-1.52656900
Cl	3.52304100	0.39621700	-0.23757600
Cl	2.22500000	-1.23617500	1.89213300
H	0.04128300	-2.20067100	0.92956700

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.8 Electronic structures fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory

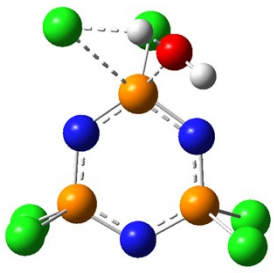
Section 5.8.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the cam-B3LYP/6-311+G(d,p) level of theory

Table S126. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

P	0.61512600	-1.37093100	-0.03543900
P	0.51882000	1.43662400	-0.01712100
P	-1.85188200	-0.05047100	0.02511200
N	1.32389000	0.05892600	-0.04276300
N	-0.96682600	-1.36540400	0.00076000
N	-1.05903400	1.32221900	0.01745500
Cl	1.32942200	-2.45181800	1.50301900
Cl	-3.08486400	-0.10286900	1.61922300
Cl	1.07982000	2.54698800	-1.60607600
Cl	1.15730400	2.54335500	1.53628600
Cl	-3.14493300	-0.08515100	-1.52237200
Cl	1.24946900	-2.41896400	-1.63912600
H	4.66944900	0.17805700	-0.57151500
O	4.27622400	0.15846400	0.30385200
H	3.32070400	0.12651000	0.15729000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S127. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.



P	-1.22588800	-0.81447900	0.08837400
P	1.62583500	-0.75039700	-0.14211100
P	0.24062400	1.62413300	0.09021200
N	0.22531600	-1.48399000	-0.18156600
N	-1.06931400	0.75265200	0.28391900
N	1.60588900	0.83322300	-0.08262100
Cl	-2.04390500	-1.65984500	1.71185600
Cl	0.38096200	2.88562200	1.65259400
Cl	2.69428900	-1.33599500	-1.75795800
Cl	2.74975400	-1.46826000	1.38093000
Cl	0.01049000	2.88211600	-1.47326500
Cl	-3.56850100	-0.17618700	-0.82279000
H	-2.71119800	-1.67643300	-1.52567800
O	-1.85808900	-2.08500200	-1.14714500
H	-1.15840000	-2.41230000	-1.73566100

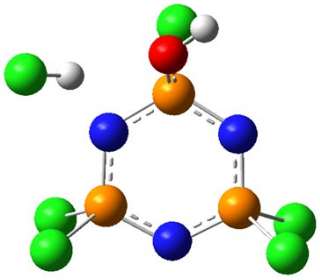
Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S128. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

P	-0.61227900	-1.21426900	0.60400600
P	1.76973600	-0.41075400	-0.60032400
P	-0.06673200	1.49837600	0.30760900
N	0.75701700	-1.53893900	-0.13310200
N	-1.01847300	0.30667800	0.74322800
N	1.31893800	1.08629700	-0.34574100
Cl	-0.59484100	-2.10713400	2.42269500
Cl	0.28543500	2.69899500	1.89149400
Cl	2.18319200	-0.66982200	-2.56038600
Cl	3.57425500	-0.71365300	0.25481800
Cl	-1.06985900	2.71821200	-0.94398400
Cl	-4.60802500	-0.61252100	-1.32094300
H	-3.50270100	-0.98994100	-0.77178500
O	-1.83229700	-1.94394300	-0.13100600
H	-1.69483400	-2.87635800	-0.34303100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S129. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.



P	-0.42332700	-1.45643400	0.27094500
P	1.86098600	-0.07739800	-0.53476900
P	-0.34675800	1.32087500	0.47160500
N	1.03195200	-1.41856900	-0.36338000
N	-1.11356100	-0.06469800	0.58027500
N	1.13921800	1.25747500	-0.07986500
Cl	-0.36456600	-2.60864700	1.93904400
Cl	-0.33856600	2.24271300	2.26789300
Cl	2.44816700	0.09125800	-2.46043200
Cl	3.62716800	-0.23507000	0.43164700
Cl	-1.44070400	2.58096000	-0.65596900
Cl	-4.38456100	-0.50512800	-1.34181400
H	-3.25040600	-0.87301500	-0.85547000
O	-1.45314200	-2.23327500	-0.66443200
H	-1.18917600	-3.10932200	-0.97129400

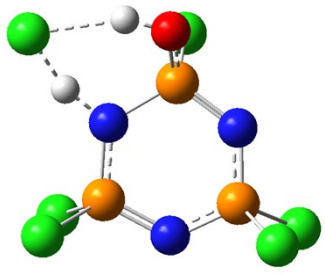
Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S130. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

P	-0.56281600	-1.40978800	-0.11762700
P	1.94492800	-0.19333100	-0.25466300
P	-0.32005700	1.36838400	0.26191200
N	0.99438100	-1.44994200	-0.37601800
N	-1.20676700	0.05817200	0.05725700
N	1.23950800	1.18829000	0.08665700
Cl	-1.00477100	-2.48645600	1.54211500
Cl	-0.70004900	2.18397700	2.07125100
Cl	3.01478200	0.00311200	-1.95280800
Cl	3.37997600	-0.54550700	1.11937500
Cl	-1.00509200	2.79074300	-0.99373000
Cl	-4.12333100	-0.50948400	-0.88930600
H	-3.01756500	-0.00040600	-0.38752100
O	-1.29841800	-2.17809200	-1.28157900
H	-2.26153900	-2.04801000	-1.32668800

Color code: P = orange, N = blue, Cl = green, O = red, H = white

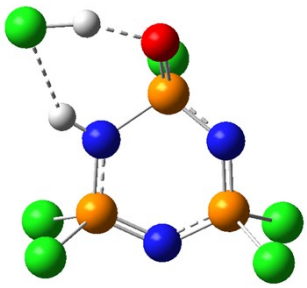
Table S131. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.



P	-0.52176900	-1.49845800	-0.13427300
P	1.90817500	-0.10760600	-0.27707800
P	-0.42624300	1.34985800	0.32380600
N	1.01629400	-1.39746100	-0.44909200
N	-1.24426400	-0.02235900	0.04864800
N	1.12908900	1.20654700	0.16673300
Cl	-0.78791800	-2.53028000	1.57786400
Cl	-0.87040200	2.05843100	2.15177600
Cl	2.91310200	0.24850900	-1.98289300
Cl	3.38530600	-0.44613900	1.04733600
Cl	-1.18986900	2.74167900	-0.89878100
Cl	-3.76684600	-0.57794700	-1.04800800
H	-2.41938200	-0.08061400	-0.34157800
O	-1.32957100	-2.25814700	-1.22252500
H	-2.27166500	-1.92050500	-1.33306500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S132. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.



P	-0.68208300	-1.48727100	-0.10423300
P	1.88237200	-0.30954400	-0.37785700
P	-0.21173300	1.45239400	0.29314100
N	0.82508000	-1.43729400	-0.60329500
N	-1.19387700	0.16616900	0.04217600
N	1.29176200	1.08998300	0.13246100
Cl	-0.65063700	-2.12010900	1.84252400
Cl	-0.56865700	2.25087600	2.10346500
Cl	2.91998900	0.00394600	-2.07313200
Cl	3.32060800	-0.85400400	0.92649100
Cl	-0.83165400	2.90256500	-0.95438400
Cl	-4.31029000	-0.68843500	-1.03054800
H	-2.20196400	0.30587500	-0.03540900
O	-1.71507400	-2.21642600	-0.86140500
H	-3.31562400	-1.55240800	-1.08358000

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.8.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the cam-B3LYP/6-311+G(d,p) level of theory

Table S133. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

P	0.03230300	1.68928200	-0.56078800
P	-1.41843600	-0.60667000	0.05233000
P	1.37534200	-0.68063400	0.05299300
N	-1.33408700	0.90885400	-0.39292600
N	1.36712500	0.83421400	-0.40711000
N	-0.03953900	-1.35963000	0.27509500
Cl	0.10742800	3.22792000	0.76470800
Cl	2.47680400	-0.88772300	1.73674800
Cl	-2.53176900	-1.63176300	-1.28555800
Cl	-2.52900700	-0.76419800	1.73344400
Cl	2.44271000	-1.76810200	-1.27611500
O	-0.00413000	2.42753400	-1.96547800
H	0.81559600	2.87171100	-2.21448400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S134. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the cam-B3LYP/6-311+G(d,p) of theory.

P	-0.12475700	1.73651900	-0.66397200
P	-1.39625400	-0.66173100	0.03816500
P	1.41822900	-0.58758100	0.15310000
N	-1.40032300	0.81070700	-0.52465300
N	1.33101700	0.91361500	-0.42479700
N	0.02286000	-1.25227800	0.45319000
Cl	-0.31553500	3.25546100	0.64480800
Cl	2.54109700	-0.65436000	1.82488400
Cl	-2.27446500	-1.89638800	-1.29457300
Cl	-2.61732600	-0.80993900	1.63516200
Cl	2.50972400	-1.67098600	-1.15190500
O	0.39075600	2.25833100	-2.00601600
H	1.40140600	1.51655700	-1.57987100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S135. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

P	-0.18744400	1.74941700	-0.92484500
P	-1.39641700	-0.64050600	0.03002600
P	1.41648300	-0.59307300	0.10285700
N	-1.37137300	0.69085500	-0.77944700
N	1.27721800	0.81191700	-0.72439500
N	0.03842800	-1.19733600	0.48696700
Cl	-0.19543900	2.86865200	0.80346800
Cl	2.57009100	-0.32771000	1.73209400
Cl	-2.32950200	-2.07496600	-1.03209200
Cl	-2.53100400	-0.52278600	1.69580300
Cl	2.54935600	-1.82056700	-1.02532000
O	-0.03517600	2.59949200	-2.10436500
H	2.10261600	1.24385000	-1.12473600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

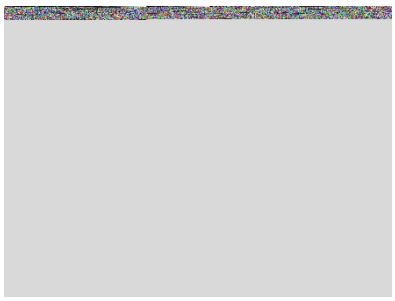
Section 5.8.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the cam-B3LYP/6-311+G(d,p) level of theory

Table S136. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

N	-0.00003600	-1.23576400	1.34365200
N	-0.00004800	1.10341700	0.00000000
N	-0.00003600	-1.23576400	-1.34365200
P	-0.00002800	0.34410600	1.40698300
P	-0.00000500	-2.07723900	0.00000000
P	-0.00002800	0.34410600	-1.40698300
Cl	1.57145800	0.98483500	2.49078300
Cl	1.57140700	-3.33928600	0.00000000
Cl	-1.57147100	0.98484800	2.49082900
Cl	-1.57131800	-3.33939900	0.00000000
Cl	1.57145800	0.98483500	-2.49078300
Cl	-1.57147100	0.98484800	-2.49082900
Cl	0.00004200	4.34910400	0.00000000
H	-0.00000200	3.04581500	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S137. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.



N	-1.90734200	-0.13362700	0.00000000
N	0.44481300	1.19728000	0.00000000
N	0.43937400	-1.37330200	0.00000000
P	-1.21214700	1.25372400	0.00000000
P	-1.09912200	-1.52309300	0.00000000
P	1.48632900	-0.15284700	0.00000000
Cl	-1.74683600	2.38766200	1.56906000
Cl	-1.74683600	-2.60996900	1.57097700
Cl	-1.74683600	2.38766200	-1.56906000
Cl	-1.74683600	-2.60996900	-1.57097700
Cl	2.51229100	-0.58019800	1.68772000
Cl	2.51229100	-0.58019800	-1.68772000
Cl	3.05349900	1.98319100	0.00000000
H	0.99367000	2.07171300	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S138. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

N	-1.85134600	0.51816900	-0.00017900
N	0.80921400	1.05824200	-0.00013000
N	0.02687600	-1.35173700	0.00025000
P	-0.75643200	1.61243800	-0.00027100
P	-1.47751400	-1.05294900	0.00009500
P	1.44564600	-0.55428000	0.00015200
Cl	-0.90767100	2.86764600	1.56728600
Cl	-2.43637400	-1.89209300	1.57033900
Cl	-0.90752400	2.86723000	-1.56817400
Cl	-2.43616800	-1.89258300	-1.57001400
Cl	2.12892600	-1.40484200	1.74113800
Cl	2.12901500	-1.40539400	-1.74053000
Cl	3.45289000	0.65893400	0.00001300
H	1.53868300	1.76787800	-0.00022100

Color code: P = orange, N = blue, Cl = green, H = white

Table S139. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

N	-1.94164300	0.00074300	-0.04212200
N	0.44183900	1.26428900	-0.16820100
N	0.40896800	-1.25586800	-0.09354900
P	-1.19697500	1.36352500	-0.07149100
P	-1.12757200	-1.38584300	-0.04248600
P	1.56329800	-0.12618000	-0.02170800
Cl	-1.66405100	2.50898000	1.52463800
Cl	-1.73386200	-2.44905200	1.56477100
Cl	-1.78721900	2.52838000	-1.60739800
Cl	-1.82287400	-2.49310000	-1.57993500
Cl	2.12511100	-0.13163200	1.94515300
Cl	2.91543600	-1.43721400	-0.97289500
Cl	3.03396400	1.47440300	-0.61298700
H	0.92399700	2.15033800	-0.28053000

Color code: P = orange, N = blue, Cl = green, H = white

Table S140. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the cam-B3LYP/6-311+G(d,p) level of theory.

N	-1.74796400	0.67540500	-0.17524200
N	-0.12278300	-1.35815300	0.33882900
N	0.91723600	1.00047700	0.04114600
P	-1.62108200	-0.87337100	0.00985200
P	-0.50048900	1.65442700	-0.04404500
P	1.55978400	-0.44567400	0.07450900
Cl	-2.38194100	-1.81789700	-1.61503700
Cl	-0.56326900	2.93674400	-1.59389800
Cl	-2.83922100	-1.55750900	1.47316100
Cl	-0.77252200	2.86464900	1.54864800
Cl	1.77698600	-1.61459300	-1.62984000
Cl	3.54978900	0.31382600	-0.15917400
Cl	2.11918000	-1.41433800	1.82309100
H	-0.01168500	-2.33981600	0.56396600

Color code: P = orange, N = blue, Cl = green, H = white

Section 5.9 Electronic structures fully optimized at the PBE0/6-311+G(d,p) level of theory

Section 5.9.1. Cartesian Coordinates for the pivotal structure in the hydrolysis reaction followed by HCl-catalyzed tautomerization at the PBE0/6-311+G(d,p) level of theory

Table S141. Cartesian coordinates (in Angstrom, Å) of the reactants (**R**) for the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	0.61149000	-1.36941000	-0.03225100
P	0.51697000	1.43272200	-0.01410500
P	-1.84852200	-0.05009900	0.02423900
N	1.33304100	0.05765000	-0.03475600
N	-0.97476700	-1.37775900	0.00421200
N	-1.06624400	1.33355700	0.02013200
Cl	1.32419700	-2.45222600	1.50136300
Cl	-3.08524700	-0.10141400	1.61134500
Cl	1.07888200	2.53593500	-1.60380200
Cl	1.15434500	2.54036800	1.53488000
Cl	-3.13258900	-0.08419200	-1.52690100
Cl	1.24449600	-2.41083400	-1.63694100
H	4.65273900	0.18126500	-0.58877000
O	4.29044400	0.16267100	0.29812600
H	3.33345400	0.12730000	0.17181400

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S142. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS**) for the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-1.19220800	-0.85303900	0.12019300
P	1.64110500	-0.71362600	-0.17451600
P	0.20806400	1.61532900	0.10027400
N	0.25816700	-1.49476400	-0.21596100
N	-1.06621700	0.71306600	0.39796200
N	1.59693200	0.87453600	-0.14474600
Cl	-2.00668000	-1.71126100	1.73226200
Cl	0.39414900	2.90099500	1.63266700
Cl	2.72340500	-1.29764600	-1.77234000
Cl	2.76496400	-1.38604800	1.36668600
Cl	-0.14586500	2.83757000	-1.46507200
Cl	-3.52772700	-0.17784200	-0.85846400
H	-2.71537000	-1.65858200	-1.42487500
O	-1.86499300	-2.14295900	-1.07725600
H	-1.17946900	-2.39559100	-1.71468500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S143. Cartesian coordinates (in Angstrom, Å) of the products with one hydrogen bond (**P_1HB**) for the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.57342300	-1.24205700	0.61426700
P	1.75251200	-0.36399900	-0.62744000
P	-0.11488800	1.47895400	0.33251600
N	0.77977600	-1.53700400	-0.17186400
N	-1.04363200	0.26332700	0.76785500
N	1.28061400	1.12603200	-0.34431400
Cl	-0.46338100	-2.13010900	2.42985200
Cl	0.22647600	2.66537400	1.92540500
Cl	2.14161300	-0.58037400	-2.59389200
Cl	3.57347700	-0.63356900	0.19653800
Cl	-1.16561800	2.68366900	-0.88846100
Cl	-4.52689500	-0.65135600	-1.35589500
H	-3.44328000	-1.04895700	-0.77828500
O	-1.79510700	-2.01007800	-0.07957000
H	-1.63264800	-2.94218700	-0.26731900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S144. Cartesian coordinates (in Angstrom, Å) of the hydrogen bond configuration change transition state (**TS_HB**) for the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.42598000	-1.44423300	0.29738600
P	1.84289100	-0.08708100	-0.55726500
P	-0.33638900	1.32454200	0.47415400
N	1.01264000	-1.43230000	-0.38464600
N	-1.12571600	-0.05155900	0.59938000
N	1.14835300	1.26410900	-0.09308800
Cl	-0.31914700	-2.56215200	1.98325900
Cl	-0.29905600	2.24972700	2.26473900
Cl	2.40510700	0.07738300	-2.48699000
Cl	3.61679700	-0.25747900	0.38660000
Cl	-1.43424800	2.58502300	-0.64311900
Cl	-4.38977000	-0.52781100	-1.35884800
H	-3.26367900	-0.92261500	-0.87436500
O	-1.47995700	-2.23995400	-0.59757600
H	-1.20602700	-3.11766300	-0.88656500

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S145. Cartesian coordinates (in Angstrom, Å) of the products with two hydrogen bonds (**P_2HB**) for the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.56014100	-1.40845300	-0.14307100
P	1.93345800	-0.18536500	-0.25846700
P	-0.33370200	1.36366000	0.26284300
N	0.99469900	-1.44943600	-0.43760000
N	-1.22471200	0.05867800	0.01102100
N	1.23388300	1.19679000	0.11244000
Cl	-0.95808700	-2.44899900	1.54692100
Cl	-0.74008500	2.13540800	2.08138000
Cl	3.02602700	0.05470100	-1.93144100
Cl	3.34397900	-0.57020400	1.12792200
Cl	-1.00196600	2.80578200	-0.97134600
Cl	-4.07613000	-0.53674100	-0.89794800
H	-2.94777600	-0.02696100	-0.41666000
O	-1.31184500	-2.20046400	-1.27992800
H	-2.27235200	-2.03828900	-1.30780200

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S146. Cartesian coordinates (in Angstrom, Å) of the synchronous proton transfer transition state (**SPT_TS**) after the hydrolysis reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.51962600	-1.49525500	-0.15643100
P	1.89166500	-0.10090300	-0.29583900
P	-0.43657800	1.34513700	0.33682500
N	1.00412200	-1.38420200	-0.55568000
N	-1.25641000	-0.02069400	0.02674200
N	1.12568700	1.20612500	0.20647800
Cl	-0.68139600	-2.47658100	1.59657100
Cl	-0.90150900	2.02712000	2.16507500
Cl	2.91803300	0.32693900	-1.96707600
Cl	3.34662400	-0.50264800	1.03244900
Cl	-1.18195600	2.75136700	-0.87632500
Cl	-3.76053200	-0.63226600	-1.06369500
H	-2.40705000	-0.08594400	-0.35304000
O	-1.37369800	-2.28205000	-1.18263600
H	-2.31655900	-1.89777700	-1.27595100

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S147. Cartesian coordinates (in Angstrom, Å) of the final product (**P**) after the HCl-catalyzed tautomerization fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.66622300	-1.48316300	-0.15396000
P	1.87558600	-0.29318400	-0.36561500
P	-0.23932000	1.44297600	0.29009500
N	0.83470700	-1.42274200	-0.68575600
N	-1.20493100	0.15801900	-0.02161800
N	1.27754300	1.09445400	0.17968000
Cl	-0.60183700	-2.09726300	1.79395000
Cl	-0.65536900	2.20378700	2.10003100
Cl	2.96923400	0.07754400	-2.00840400
Cl	3.26349700	-0.88026600	0.97083500
Cl	-0.82156900	2.91113500	-0.94940500
Cl	-4.26412600	-0.72136800	-0.99480000
H	-2.21618900	0.28301700	-0.11209500
O	-1.69504900	-2.23808200	-0.89975000
H	-3.25242500	-1.57657900	-1.06138300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.9.2. Cartesian Coordinates for chemical species appearing in the tautomerization reaction without the interference from HCl at the PBE0/6-311+G(d,p) level of theory

Table S148. Cartesian coordinates (in Angstrom, Å) of the reactants of the tautomerization reaction without the interferences of HCl (**Tauto_R**) fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	0.03195400	1.67583800	-0.59058000
P	-1.41549400	-0.60036700	0.05565700
P	1.37177600	-0.67674200	0.05298900
N	-1.34677100	0.90524500	-0.43955900
N	1.37668300	0.82441600	-0.46346200
N	-0.04039800	-1.35830700	0.31279400
Cl	0.11432900	3.18969600	0.76029600
Cl	2.47779100	-0.83169700	1.73588800
Cl	-2.52126200	-1.66189200	-1.25472600
Cl	-2.52762000	-0.71071900	1.73553200
Cl	2.42802200	-1.80526600	-1.24442300
O	-0.00983600	2.43524500	-1.98511000
H	0.81710900	2.87555200	-2.21214600

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S149. Cartesian coordinates (in Angstrom, Å) of the tautomerization transition state without the interferences (**Tauto_TS**) fully optimized at the PBE0/6-311+G(d,p) of theory.

P	-0.16750800	1.72674000	-0.67572700
P	-1.37117900	-0.69182200	0.03829300
P	1.43238600	-0.54326400	0.16708700
N	-1.42446400	0.76292500	-0.57777100
N	1.31625800	0.95740300	-0.41550900
N	0.05492800	-1.23784600	0.50517200
Cl	-0.43044900	3.22463800	0.63985100
Cl	2.58052400	-0.58694400	1.81726900
Cl	-2.18838900	-1.98768700	-1.27007600
Cl	-2.60813500	-0.83317100	1.61986100
Cl	2.51808000	-1.61073200	-1.15320400
O	0.34768100	2.27361400	-2.00966800
H	1.36827700	1.55515400	-1.56359900

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Table S150. Cartesian coordinates (in Angstrom, Å) of the product of the tautomerization reaction without the interferences (**Tauto_P**) fully optimized at the PBE0/6-311+G(d,p) level of theory.

P	-0.21071600	1.72988400	-0.94789500
P	-1.38291700	-0.64930400	0.02478300
P	1.42481300	-0.56715800	0.10221900
N	-1.38638100	0.64876800	-0.84931800
N	1.26452000	0.80889300	-0.76960000
N	0.05429400	-1.18197600	0.51605800
Cl	-0.24297800	2.79779600	0.80883400
Cl	2.57388900	-0.24217600	1.72009400
Cl	-2.29529700	-2.12975900	-0.98304200
Cl	-2.51654400	-0.48244100	1.68416000
Cl	2.56679500	-1.81254500	-0.99086700
O	-0.06748500	2.61113100	-2.10867700
H	2.08543300	1.25492700	-1.16321300

Color code: P = orange, N = blue, Cl = green, O = red, H = white

Section 5.9.3. Cartesian Coordinates for chemical species appearing in the ring-opening reaction at the PBE0/6-311+G(d,p) level of theory

Table S151. Cartesian coordinates (in Angstrom, Å) of the reactants (**R'**) for the HCl-initiated ring-opening reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

N	0.00007900	-1.23918000	1.35538800
N	0.00010900	1.11514900	0.00000000
N	0.00007900	-1.23918000	-1.35538800
P	0.00007900	0.34524600	1.40566200
P	-0.00002500	-2.06972700	0.00000000
P	0.00007900	0.34524600	-1.40566200
Cl	1.56970300	0.98573400	2.48526800
Cl	1.56944100	-3.32892300	0.00000000
Cl	-1.56957500	0.98576600	2.48521300
Cl	-1.56979200	-3.32856600	0.00000000
Cl	1.56970300	0.98573400	-2.48526800
Cl	-1.56957500	0.98576600	-2.48521300
Cl	-0.00013200	4.31582000	0.00000000
H	-0.00001600	3.00842000	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S152. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS1**) for the HCl-initiated ring-opening reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

N	-1.91937600	-0.14518300	0.00000000
N	0.44695700	1.18466800	0.00000000
N	0.44770200	-1.39943000	0.00000000
P	-1.20830100	1.24166500	0.00000000
P	-1.09892100	-1.53035900	0.00000000
P	1.47841200	-0.16537800	0.00000000
Cl	-1.74308200	2.37176300	1.56748500
Cl	-1.74308200	-2.61525500	1.56927600
Cl	-1.74308200	2.37176300	-1.56748500
Cl	-1.74308200	-2.61525500	-1.56927600
Cl	2.52509000	-0.56399000	1.67339600
Cl	2.52509000	-0.56399000	-1.67339600
Cl	3.01489400	2.04316100	0.00000000
H	1.02850700	2.05132100	0.00000000

Color code: P = orange, N = blue, Cl = green, H = white

Table S153. Cartesian coordinates (in Angstrom, Å) of the intermediate (**Int**) for the HCl-initiated ring-opening reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

N	-1.87944700	0.43332700	-0.26696200
N	0.76465900	1.10120600	-0.12997800
N	0.06824100	-1.26470500	0.42470800
P	-0.82991000	1.57250700	-0.11382500
P	-1.41281400	-1.09158000	0.02722100
P	1.46243500	-0.46377000	0.11782900
Cl	-1.10517500	2.68536500	1.54611800
Cl	-2.60360900	-1.83404300	1.46864500
Cl	-0.98087300	2.92795900	-1.58134900
Cl	-1.98511700	-2.16221300	-1.59408000
Cl	2.30207100	-0.99504500	1.90719000
Cl	2.01181900	-1.60910100	-1.50107700
Cl	3.39456300	0.75316500	-0.26748200
H	1.45760900	1.83035300	-0.28817400

Color code: P = orange, N = blue, Cl = green, H = white

Table S154. Cartesian coordinates (in Angstrom, Å) of the transition state (**TS2**) for the HCl-initiated ring-opening reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

N	-1.95603800	0.00213600	-0.03448600
N	0.44431700	1.25961000	-0.18219300
N	0.41439000	-1.26558400	-0.15783500
P	-1.19427900	1.36137000	-0.07079700
P	-1.12546400	-1.37994600	-0.05074700
P	1.56296600	-0.12754300	-0.04156900
Cl	-1.64134700	2.50523500	1.52871300
Cl	-1.68420600	-2.42867500	1.58131000
Cl	-1.79400600	2.52662900	-1.59870800
Cl	-1.86180600	-2.49635600	-1.55595500
Cl	2.09310600	-0.17979000	1.93134600
Cl	2.92020500	-1.40889600	-1.00705500
Cl	3.03293900	1.48604200	-0.56523600
H	0.92992500	2.14740500	-0.27673900

Color code: P = orange, N = blue, Cl = green, H = white

Table S155. Cartesian coordinates (in Angstrom, Å) of the products (**P'**) for the HCl-initiated ring-opening reaction fully optimized at the PBE0/6-311+G(d,p) level of theory.

N	-1.75653600	0.63655800	-0.28628300
N	-0.09562400	-1.30736600	0.45398900
N	0.91323000	1.04308200	0.03532200
P	-1.58836600	-0.89837300	0.00017300
P	-0.53321100	1.64171400	-0.07490300
P	1.56055000	-0.40719300	0.09815100
Cl	-2.23272300	-1.94268800	-1.60856200
Cl	-0.59114900	2.95841400	-1.58863900
Cl	-2.85147100	-1.54827800	1.43552100
Cl	-0.88936200	2.79851600	1.54008600
Cl	1.74034200	-1.62771600	-1.57169000
Cl	3.52803300	0.36271800	-0.21161700
Cl	2.17630300	-1.31737200	1.85656500
H	0.02836300	-2.26924700	0.74919900

Color code: P = orange, N = blue, Cl = green, H = white