Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

The nature of intermolecular interactions in pyridinium – anion – β-hexachlorocyclohexane molecular crystals

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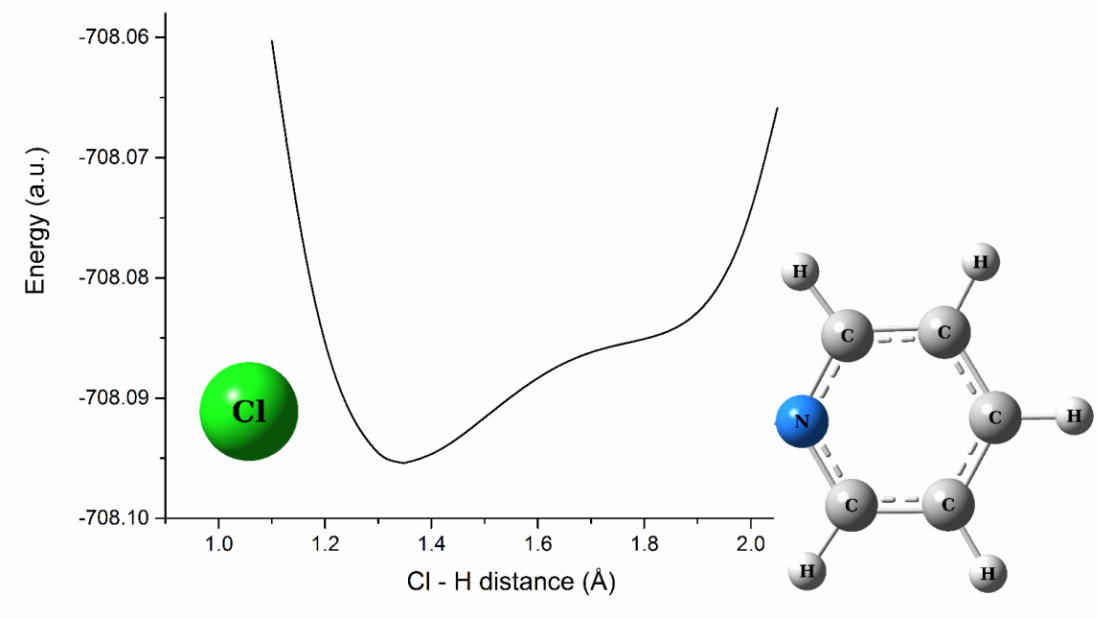

Figure S1. The potential energy surface (1D curve) of the H atom displacement between the chlorine and nitrogen atoms inside the HCl – pyridine molecular complex obtained at DF-LMP2/aug-cc-pVTZ level of theory.

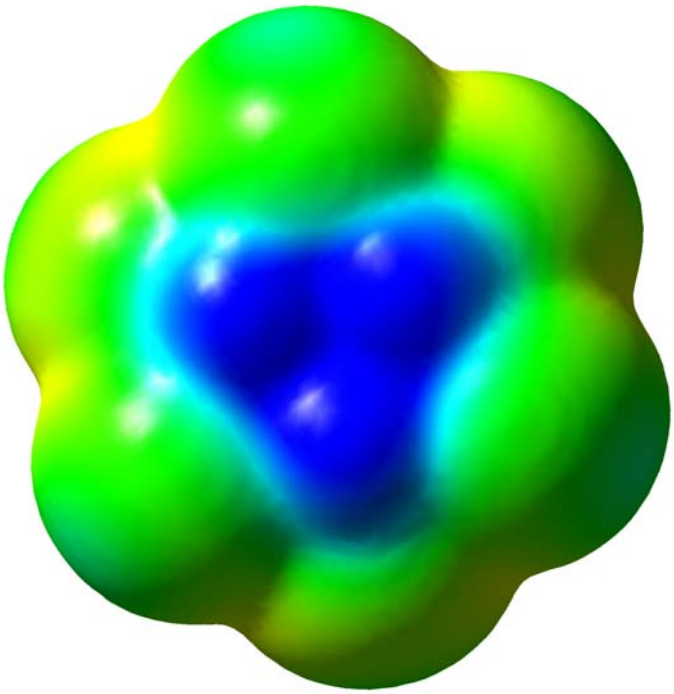

Figure S2. The molecular electrostatic potential map of the β-hexachlorocyclohexane (β-HCH).

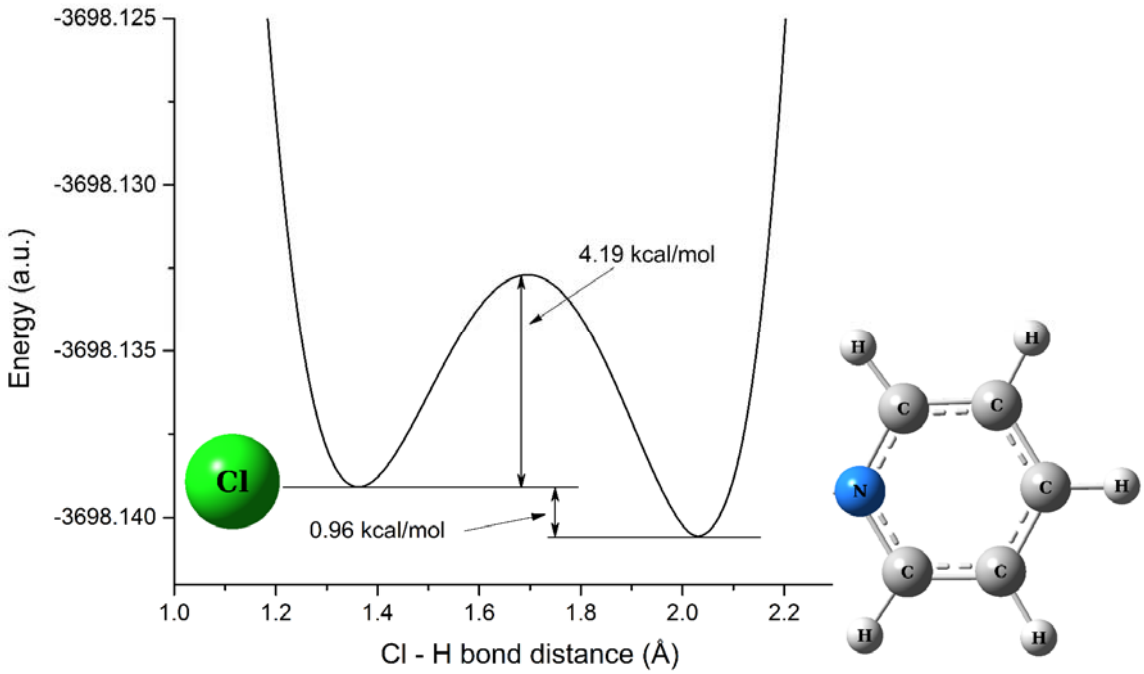

Figure S3. The potential energy surface (1D curve) of the H atom displacement between the chlorine and nitrogen atoms inside the β-HCH ··· Cl^- ··· H^+Py molecular complex obtained at DF-LMP2/aug-cc-pVTZ level of theory.

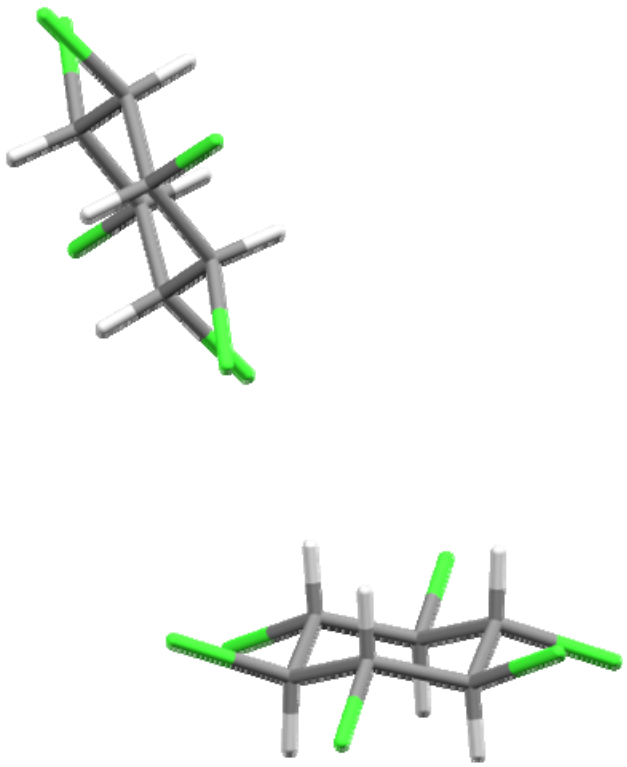

Figure S4. The geometry structure of the β-HCH optimized dimer.

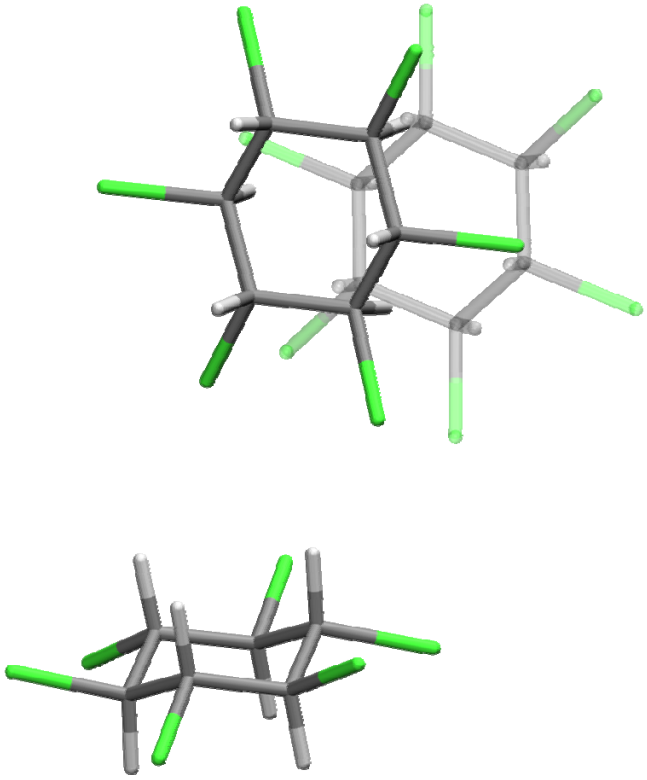

Figure S5. The structural difference between the optimized (opaque) and the crystal (transparent) geometry structures of the β-HCH dimer configuration.

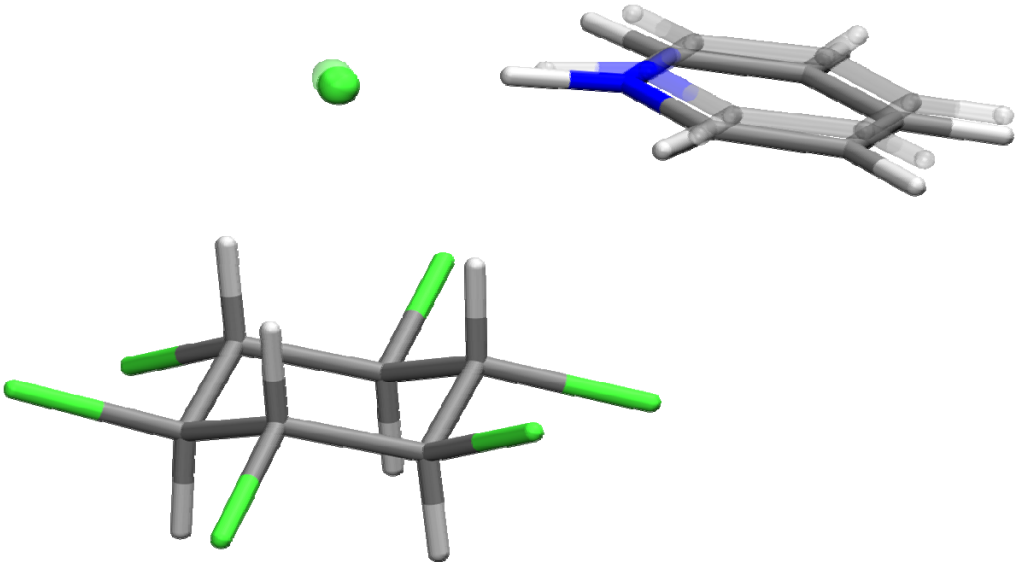

Figure S6. The structural difference between the optimized (opaque) and the crystal (transparent) geometry structures of the β-HCH ··· Cl^- ··· H^+Py cluster configuration.

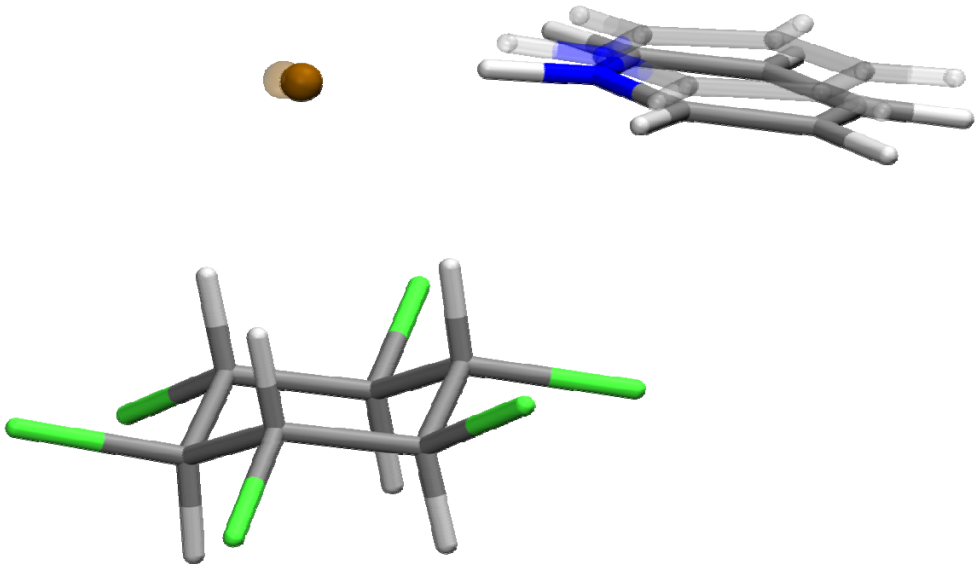

Figure S7. The structural difference between the optimized (opaque) and the crystal (transparent) geometry structures of the β-HCH ··· Br^- ··· H^+Py cluster configuration.

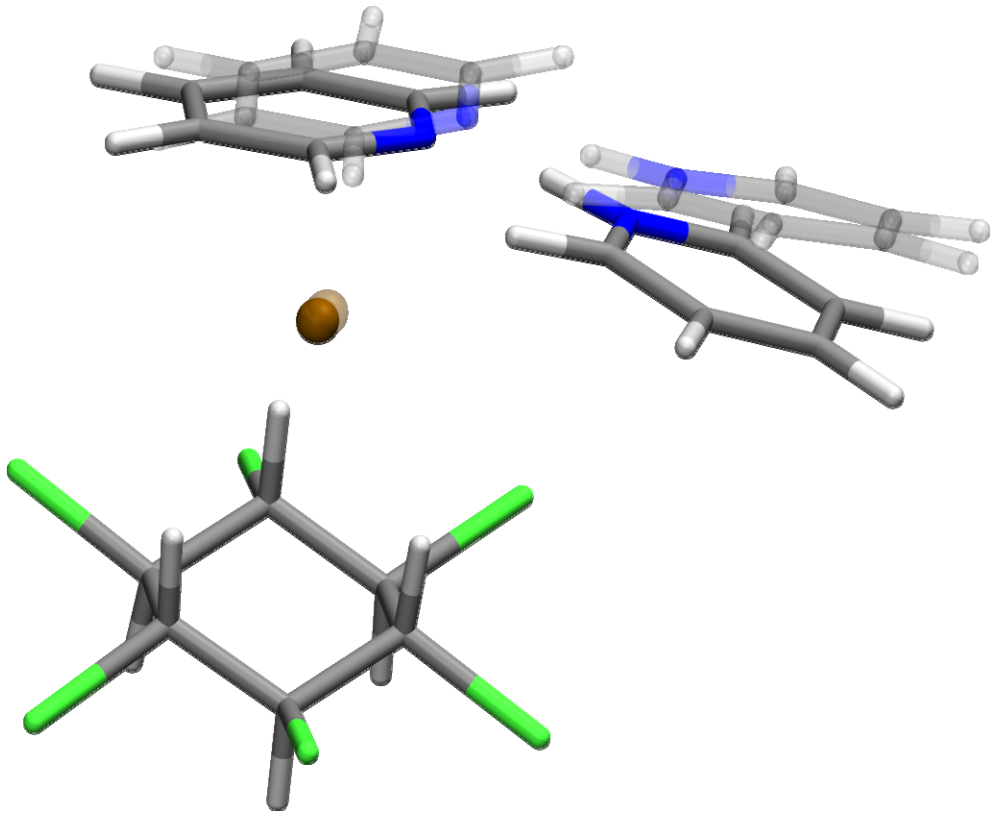

Figure S8. The structural difference between the optimized (opaque) and the crystal (transparent) geometry structures of the β-HCH ··· Br^- ··· PyH^+Py cluster configuration.

Table S1. The X···H, X···H^+ intermolecular and H^+-N bond distances (in Å) for different cluster configurations obtained at DF-LMP2/def2-TZVP level of theory.

Structure	X···H (β-HCH)	X···H^+ (Py)	H^+-N (Py)
β-HCH ··· Cl^- (optimized)	2.439 2.439 2.441	-	-
β-HCH ··· Cl^- + H^+Py (crystal)	2.616 2.789 2.789	2.041	1.093
β-HCH ··· Cl^- + H^+Py (optimized)	2.522 2.751 2.758	1.699	1.144
β-HCH ··· Br^- (optimized)	2.627 2.628 2.642	-	-
β-HCH ··· Br^- + H^+Py (crystal)	2.755 2.890 2.890	2.167	1.087
β-HCH ··· Br^- + H^+Py (optimized)	2.660 2.957 2.966	1.909	1.111
β-HCH ··· Br^- + PyH^+Py (crystal)	2.905 2.817 2.742	4.581	1.107 1.590
β-HCH ··· Br^- + PyH^+Py (optimized)	2.688 2.751 2.754	4.198	1.092 1.611

Table S2. The intermolecular interaction energy in *Scheme 2* partition for different cluster configurations obtained at HF, DF-LMP2, DF-LCCSD(T) and different SAPT level of theories (Subsystems are marked by red and blue colors).

Structure	Basis	Method				
		HF	DF-LMP2	DF-LCCSD(T)	SAPT[0]	SAPT[2]
(β-HCH + Cl^-) ··· H^+Py (crystal)	TZVP[a]	-92.06	-102.51	-101.76	-101.01	-101.98
	AVTZ[b]	-90.61	-102.56	-102.09	-101.82	-
(β-HCH + Cl^-) ··· H^+Py (optimized)	TZVP	-94.23	-110.14	-109.06	-109.64	-111.14
	AVTZ	-92.59	-110.11	-108.89	-110.99	-
(β-HCH + Br^-) ··· H^+Py (crystal)	TZVP	-87.86	-98.41	-97.74	-97.26	-98.06
	AVTZ	-86.84	-99.19	-98.80	-98.20	-
(β-HCH + Br^-) ··· H^+Py (optimized)	TZVP	-86.75	-101.94	-100.85	-101.52	-102.87
	AVTZ	-85.67	-103.31	-102.41	-103.07	-
(β-HCH + Br^-) ··· PyH^+Py (crystal)	TZVP	-64.77	-72.08	-72.11	-73.59	-73.42
	AVTZ	-63.85	-73.26	-73.15	-74.65	-
(β-HCH + Br^-) ··· PyH^+Py (optimized)	TZVP	-63.41	-77.84	-77.53	-80.92	-80.59
	AVTZ	-62.38	-79.97	-79.57	-83.23	-

[a]Def2-TZVP; [b]Aug-cc-pVTZ

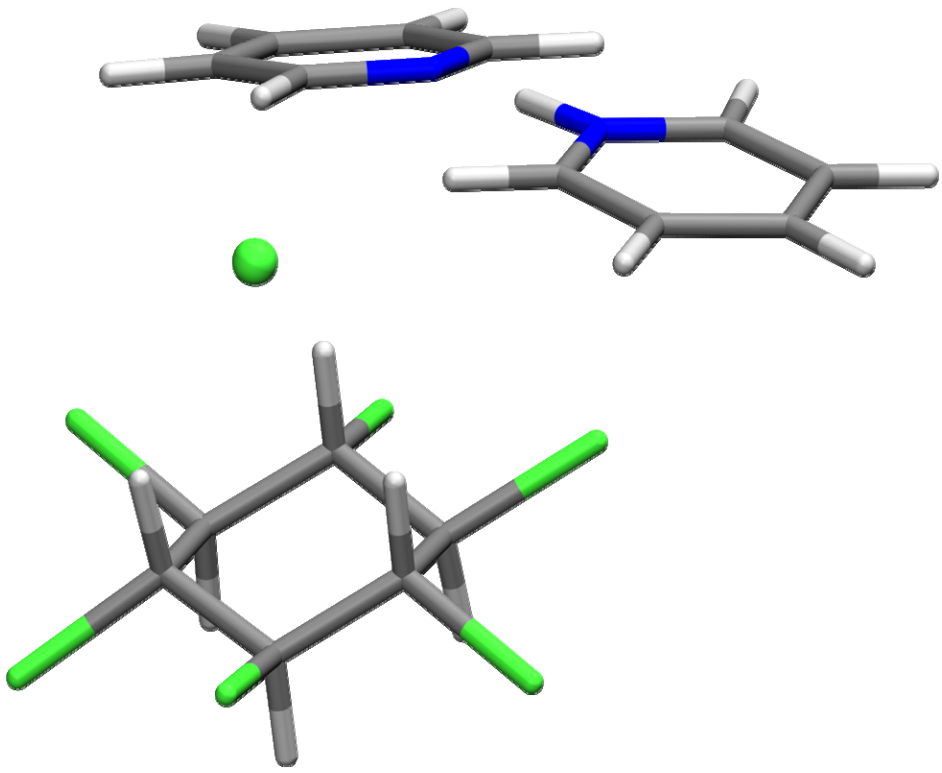

Figure S9. The optimized geometry structure of the β-HCH ··· Cl^- ··· PyH^+Py cluster configuration.