Electronic Supplementary Material (ESI) for ChemComm.

Supramolecular anion recognition by β-HCH

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Supplementary information

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1. **X-ray data**

1.1. **Single crystal X-ray diffractometry general experimental conditions**

The details of the crystal structures determination and refinement are given in Tables 1. The crystals of **1** and **2** were mounted on cryoloops and data were collected with a Bruker SMART APEX diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature (297 K). The data for crystals of **3** and **4**were collected on Oxford Diffraction SuperNova dual wavelength diffractometer with operating mirror monochromated CuKα radiation mode (λ = 1.5418 Å) at room temperature.

Single-crystal diffraction X-ray data collection was monitored and all the data were corrected for Lorentzian, polarization and absorption effects using CrysAlisPro program.[1] For structure solving and refinement the software package SHELX-2015 was used.[2] The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter, except the hydrogen atom bonded to the pyridines in compounds **4**, **3** and **2**, respectively, which were found in the difference map and were refined unrestrained.

The drawings were created with Diamond program.[3]

CCDC reference numbers: 1497418 (**4**), 1497417 (**3**), 1497419 (**1**) and 718661 (**2**).

1.2. **Solid state structure *of* β-HCH**

β-HCH (**1**) crystallizes in a high symmetry cubic form and its molecular structure shows a chair conformation exhibiting the chlorine atoms in equatorial orientations. In the lattice (Figure S1), bifurcated contacts for each chlorine atom of a molecule with H atoms of six different neighboring molecules (which are almost "coplanar") are observed. The H atoms of the same molecule give similar contact with other six molecules situated on both sides of the central reference β-HCH unit. (d_1 = 3.046 and d_2 = 3.080 Å; C-Cl---H angles are α_1 = 111.87 and α_2 = 113.08 °). The elementary cell for the crystal structure of this compound is a perfect cube.

Table 1. Crystallographic data and structure refinement details for **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_6H_6Cl_6$	$C_{16}H_{18}Cl_8N_2$	$C_{16}H_{18}Br_2Cl_6N_2$	$C_{16}H_{17}BrCl_6N_2$
Formula weight	290.81	521.92	610.84	529.93
Temperature (K)	297(2)	297(2)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073	1.54178	1.54178
Crystal system	Cubic	Monoclinic	Monoclinic	Monoclinic
Space Group	*Pa-3*	*C2/m*	*C2/m*	*P2(1)/c*
Unit cell dimensions				
a (Å)	10.0568(12)	15.0733(19)	15.078(3)	7.4262(2)
b (Å)	10.0568(12)	9.1677(11)	9.4943(19)	17.3301(5)
c (Å)	10.0568(12)	8.2639(10)	8.2367(16)	17.0948(5)
α (°)	90	90	90	90
β (°)	90	94.462(2)	96.05(3)	95.613(3)
γ (°)	90	90	90	90
Volume ($Å^3$)	1017.1(4)	1138.5(2)	1172.6(4)	2189.50(11)
Z	4	2	2	4
D_c (mg/cm^3)	1.899	1.522	1.730	1.608
Absorption coefficient (mm^{-1})	1.628	0.994	10.717	9.324
F(000)	576	528	600	1056
Crystal size (mm)	0.20 x 0.19 x 0.16	0.20 x 0.18 x 0.15	0.40 x 0.30 x 0.03	0.28 x 0.17 x 0.05
θ range for data collection (°)	3.509 to 24.902	2.472 to 24.972	5.401 to 71.342	3.641 to 71.461
Reflections collected	6638	5534	1922	7594
Independent reflections	300 [R(int) = 0.0361]	1074 [R(int) = 0.0309]	1176 [R(int) = 0.0232]	4146 [R(int) = 0.0428]
Refinement method		Full matrix least-squares on F^2		
Data / restraints / parameters	300 / 0 / 19	1074 / 0 / 70	1176 / 0 / 70	4146 / 0 / 230
Goodness-of-fit on F^2	1.562	1.179	0.953	1.000
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0351, wR_2 = 0.1681	R_1 = 0.0561, wR_2 = 0.1203	R_1 = 0.0394, wR_2 = 0.1108	R_1 = 0.0531, wR_2 = 0.1566
R indices (all data)	R_1 = 0.0352, wR_2 = 0.1681	R_1 = 0.0641, wR_2 = 0.1242	R_1 = 0.0415, wR_2 = 0.1157	R_1 = 0.0974, wR_2 = 0.1959
Largest diff. peak and hole, eA^{-3}	0.320 and -0.537	0.417 and -0.285	0.523 and -0.525	0.554 and -0.843

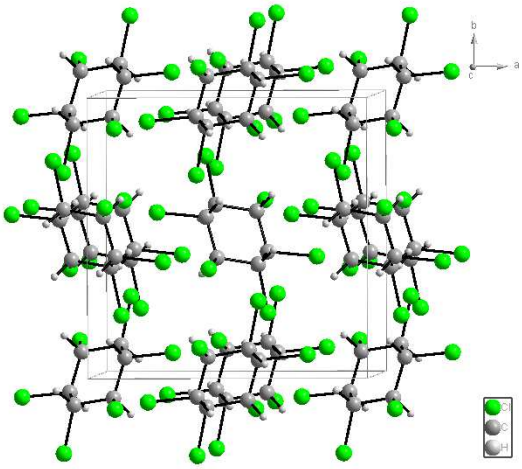


Figure S1. X-ray molecular structure of **1**: representation of the lattice.

1.3. **Details of the solid state structures of 2, 3 and 4**

In figure S2 are shown representative units for **2** and **3**.

a)

b)

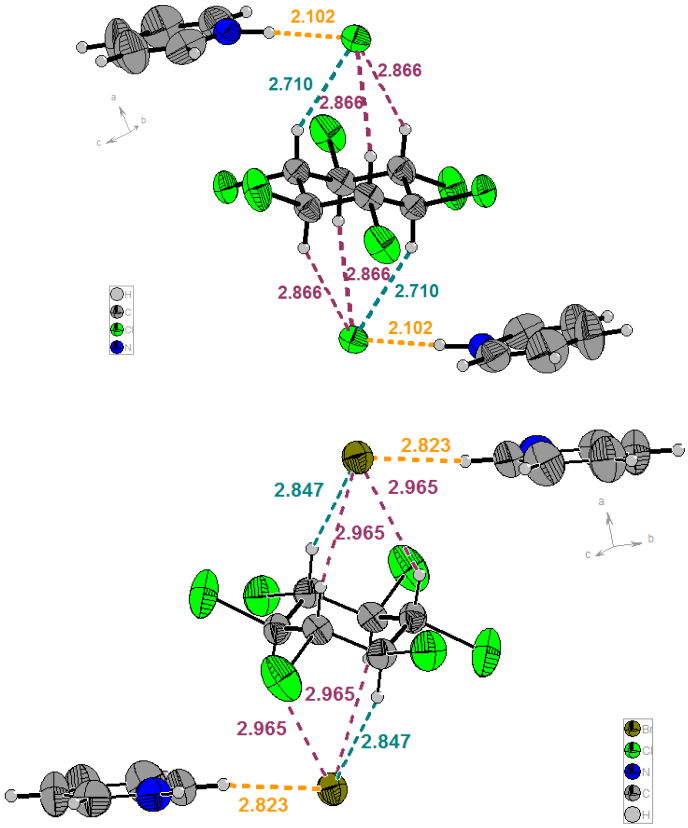


Figure S2. Representations of typical units for **2** (a) and **3** (b).

Details of the supramolecular associationsof β-HCH, piridinium and chloride units in the lattice of **2** are presented in Figure S3.

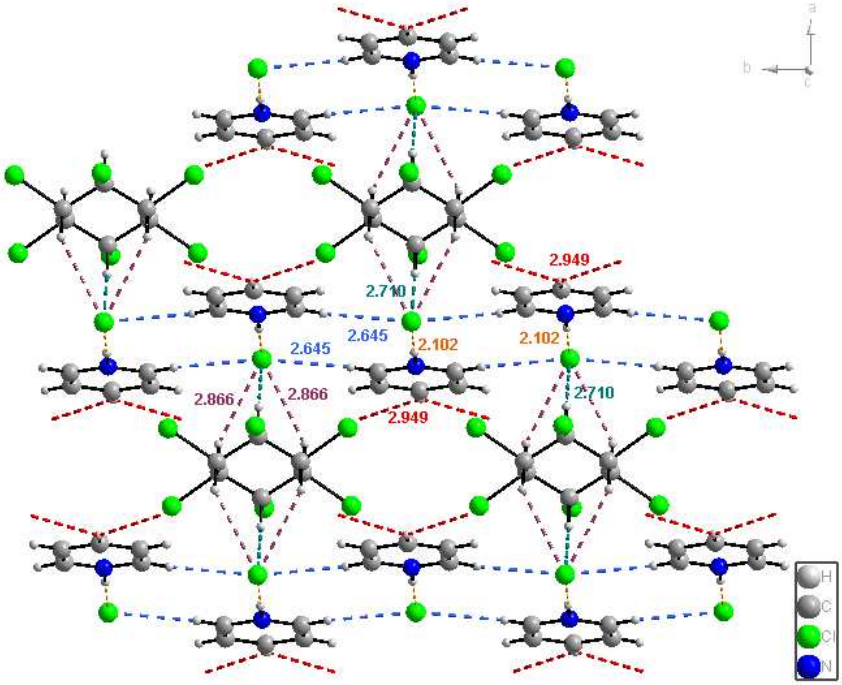


Figure S3. Representation of solid state supramolecular network of **2** [theβ sheet like ribbons (contact in ornage and blue) and the 2D structure are shown in detail, while the formation of the 3D aggregate is suggested by the contacts (in red) involving the H atom at position 4 of the pyridine units]

Details of the of crystal structure of **4** is depicted in Figure S4 showing contacts that connect “columns” in the 3D network.

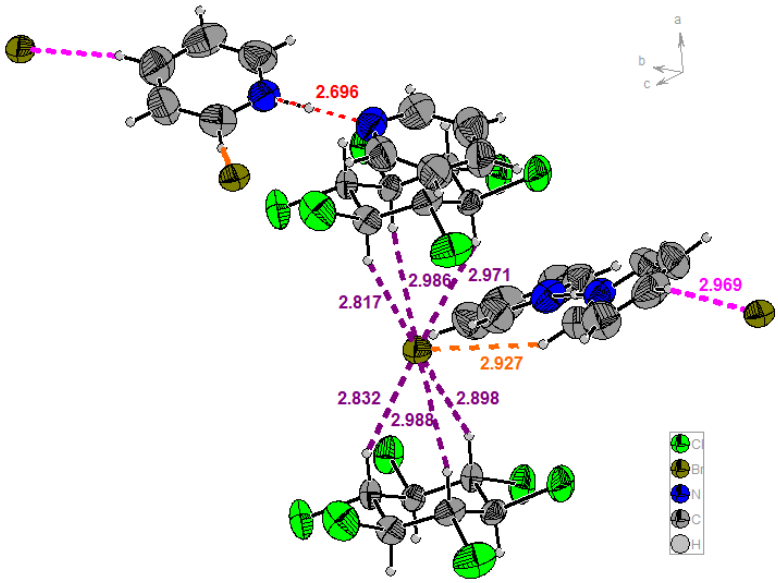


Figure S4. Representation ofa typical unit in the crystal structure of **4**.

2. ^{1}H NMR titration results and ESI-MS data

2.1.General experimental conditions

^{1}H NMR spectra were recorded at room temperature, in CD_3CN as solvent, on a 600 MHz equipment. Chemical shifts (δ) are reported in parts per million (ppm) using residual solvent peak as internal reference.

Mass Spectra (HRMS) were recorded on a LTQ ORBITRAP XL spectrometer (ThermoScientific) using negative-ion electrospray (ESI-) ionization technique. The samples were introduced into the spectrometer by direct infusion at a flow rate of 7 μL/min. The conditions used were as follows: spray voltage (5 kV for [HCH•Cl^-], 2kV for [HCH•Br^-] and 3 kV for [HCH•I^-] and [HCH•HSO_4^-]), sheath and auxiliary gas flow (20 and 5 arbitrary units, respectively), capillary temperature (275 °C), capillary voltage (- 10V for [HCH•Cl^-], -4 V for [HCH•Br^-], -5V for [HCH•I^-] and -2 V for [HCH•HSO_4^-]), tube lens voltage (-50V for [HCH•Cl^-], [HCH•Br^-] and [HCH•HSO_4^-] and - 20 V for [HCH•I^-]). The microscans were set to three.

2.2.Job plot results and calculations of the association constants values

The JOB-PLOT experiments were run using the model for fast equilibria as in the spectra there are only a set of signals at average δ values.[4]

The stoichiometry of host-guest complexes between *β*-HCH (**1**) and different anions (Cl^-, Br^-, I^- and HSO_4^-) was determined by ^{1}H NMR titration at room temperature. In each case nine NMR samples in various host/guest ratios (Table 1) were prepared using 5mM stock solutions in CD_3CN of **1** (5mM) and of the salts exhibiting the target anions **G1** (pyridimium hydrochloride), **G2** (pyridimiumhydrobromide), **G3** [tetrabutylammonium iodide (TBAI)] and **G4** [tetrabutylammoniumhydrogensulfate (TBAHS)] at a final concentration of 5 mM (host [H] + guest [G]).

The changes in the chemical shifts of the signal at 4.2560 ppm of *β*-HCH for increasing amounts of guest are indicated in Tables 2-5.

Since the binding equilibrium has a very fast exchange rate compared to the NMR time scale a modified Job plot[4] was used in order to determine the complex stoichiometry. Thus, Δδ x [H] was plotted as y-coordinate and [H]/([H]+[G]) as x-coordinate as shown in Figures S5-S12.

The obtained data suggest in all cases a 1:1 binding stoichiometry.

a) Details of the JOB-PLOT experiment run with G1

Table 1. ^{1}H NMR titration data for guest G1

HCH µL	PyxHClµL	nHCH mMx10^3	nPyxHCl mMx10^3	[HCH]/ ([HCH]+[PyHCl])	Δδ ppm	Δδ x nHCH	δexp ppm
50	450	0.25	2.25	0.1	0.0091	0.002275	4.2651
100	400	0.50	2.00	0.2	0.0084	0.0042	4.2644
150	350	0.75	1.75	0.3	0.0077	0.005775	4.2637
200	300	1.00	1.50	0.4	0.0066	0.0066	4.2626
250	250	1.25	1.25	0.5	0.0058	0.00725	4.2618
300	200	1.50	1.00	0.6	0.0047	0.00705	4.2607
350	150	1.75	0.75	0.7	0.0036	0.0063	4.2596
400	100	2.00	0.50	0.8	0.0022	0.0044	4.2582
450	50	2.25	0.25	0.9	0.0010	0.00225	4.2570

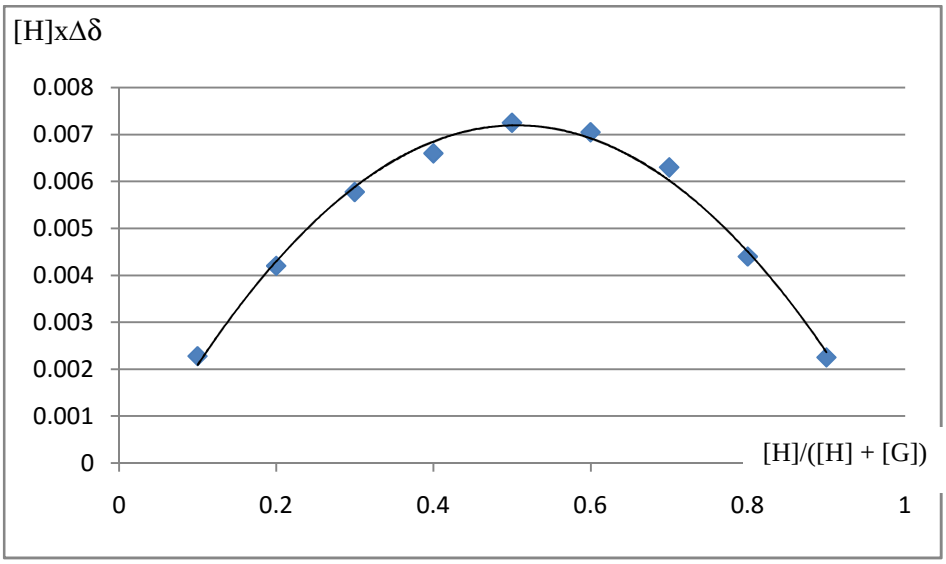


Figure S5. Job plot of **1** (5mM) with **G1** (5mM)in CD_3CN

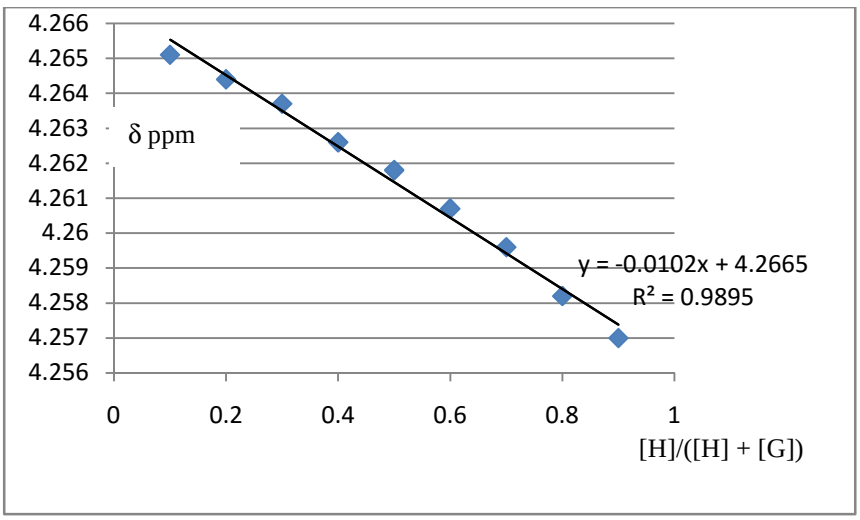


Figure S6. Determination of δ_c

b) Details of the JOB-PLOT experiment run with G2

Table 3.^{1}H NMR titration data for guest G2

HCH µL	PyxHBrµL	nHCH mMx10^{3}	nPyxHBr mMx10^{3}	[HCH]/ ([HCH]+[PyHBr])	Δδ ppm	Δδ x nHCH	δexp ppm
50	450	0.25	2.25	0.1	0.0487	0.02435	4.3047
100	400	0.50	2.00	0.2	0.042	0.042	4.298
150	350	0.75	1.75	0.3	0.0381	0.05715	4.2941
200	300	1.00	1.50	0.4	0.0321	0.0642	4.2881
250	250	1.25	1.25	0.5	0.029	0.0725	4.285
300	200	1.50	1.00	0.6	0.0224	0.0672	4.2784
350	150	1.75	0.75	0.7	0.0158	0.0553	4.2718
400	100	2.00	0.50	0.8	0.0098	0.0392	4.2658
450	50	2.25	0.25	0.9	0.0038	0.0171	4.2598

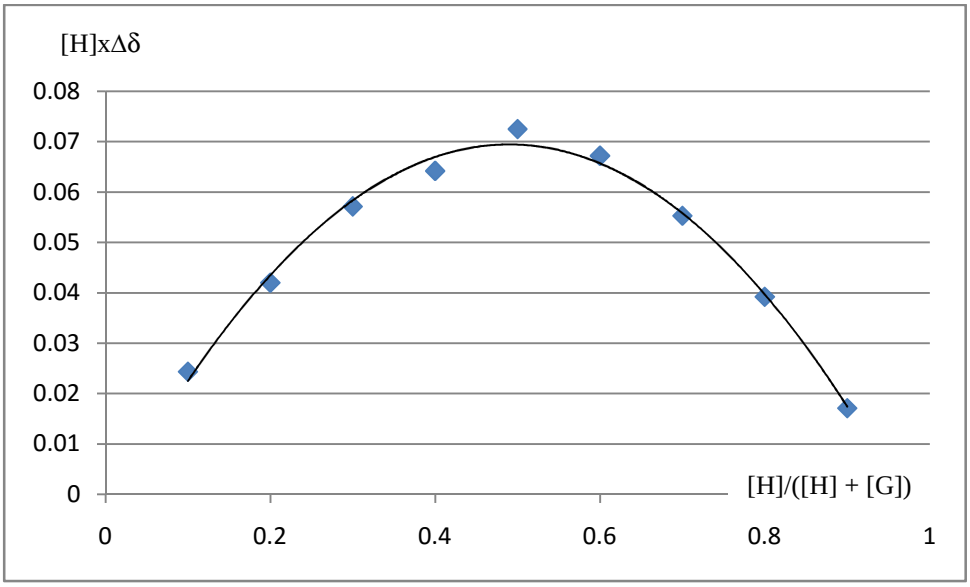


Figure S7. Job plot of **1** (5mM) with **G2** (5mM) in CD_3CN

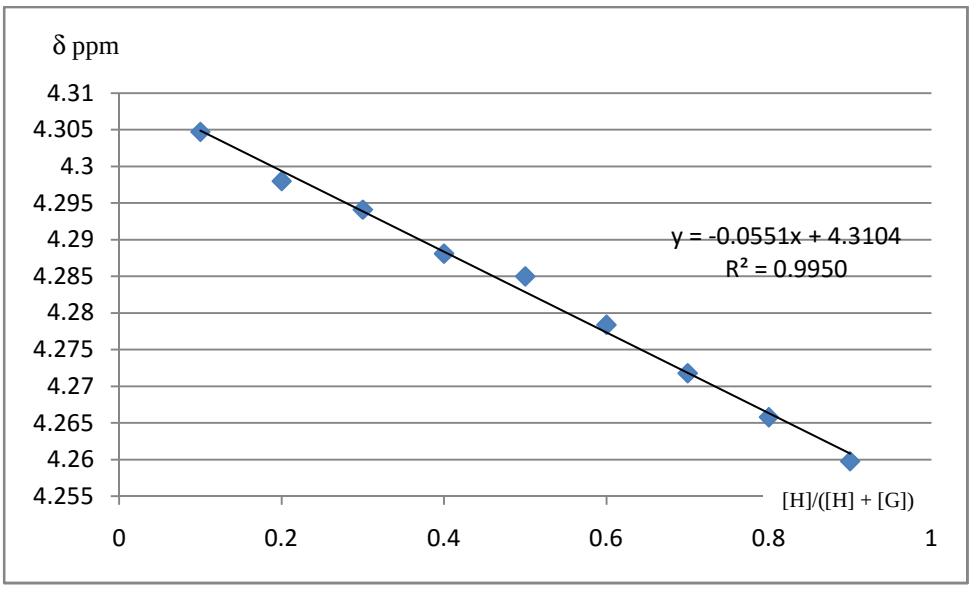


Figure S8. Determination of δ_c

c) Details of the JOB-PLOT experiment run with G3

Table 4.^{1}H NMR titration data for guest G3

HCH µL	TBAI µL	nHCH mMx10^{3}	nTBAI mMx10^{3}	[HCH]/ ([HCH]+[TBAI])	Δδ ppm	Δδ x nHCH	δexp ppm
50	450	0.25	2.25	0.1	0.0242	0.0121	4.2802
100	400	0.50	2.00	0.2	0.0212	0.0212	4.2772
150	350	0.75	1.75	0.3	0.018	0.027	4.2740
200	300	1.00	1.50	0.4	0.0161	0.0322	4.2721
250	250	1.25	1.25	0.5	0.0131	0.03275	4.2691
300	200	1.50	1.00	0.6	0.0106	0.0318	4.2666
350	150	1.75	0.75	0.7	0.0079	0.02765	4.2639
400	100	2.00	0.50	0.8	0.0052	0.0208	4.2612
450	50	2.25	0.25	0.9	0.0038	0.0171	4.2598

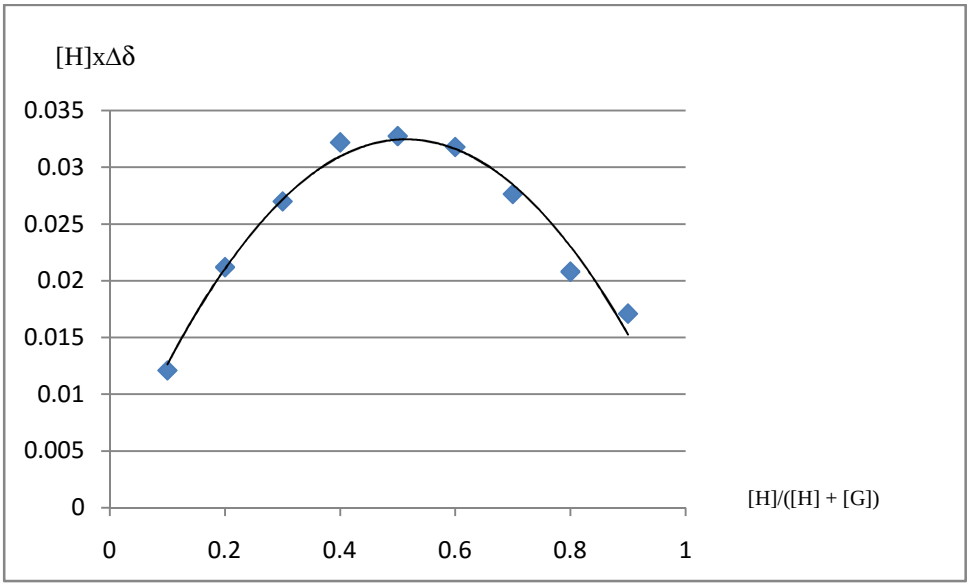


Figure S9. Job plot of **1** (5mM) with **G3** (5mM) in CD_3CN

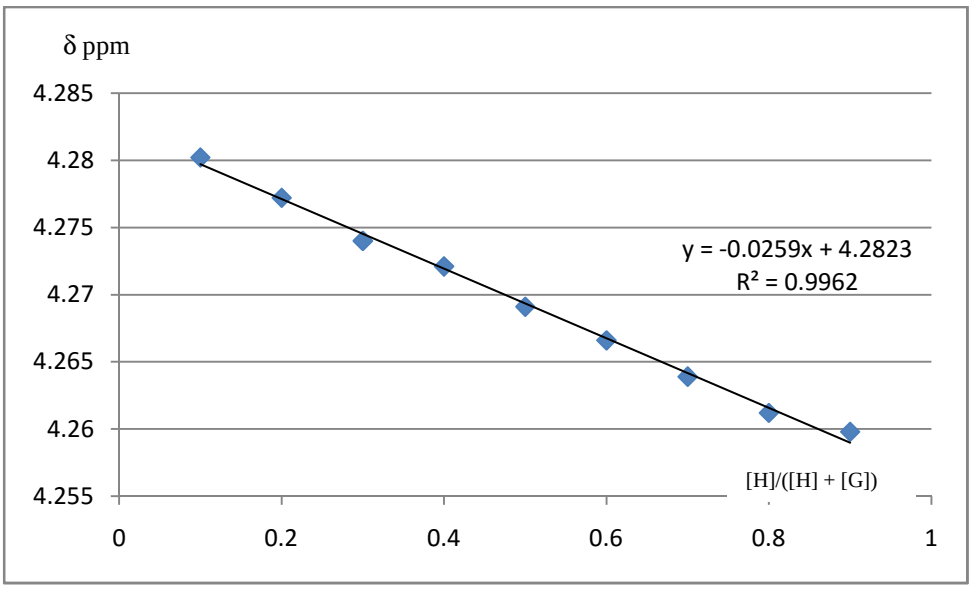


Figure S10. Determination of δ_c

d) Details of the JOB-PLOT experiment run with G4

Table 5.^{1}H NMR titration data for guest G4

HCH µL	TBAHS µL	nHCH mMx10^{3}	nTBAHS mMx10^{3}	[HCH]/ ([HCH]+[TBAHS])	Δδ ppm	Δδ x nHCH	δexp ppm
50	450	0.25	2.25	0.1	0.0095	0.00475	4.2655
100	400	0.50	2.00	0.2	0.0077	0.0077	4.2637
150	350	0.75	1.75	0.3	0.0072	0.0108	4.2632
200	300	1.00	1.50	0.4	0.0059	0.0118	4.2619
250	250	1.25	1.25	0.5	0.0053	0.01325	4.2613
300	200	1.50	1.00	0.6	0.0036	0.0108	4.2596
350	150	1.75	0.75	0.7	0.0026	0.0091	4.2586
400	100	2.00	0.50	0.8	0.001	0.004	4.257
450	50	2.25	0.25	0.9	0.0002	0.0009	4.2562

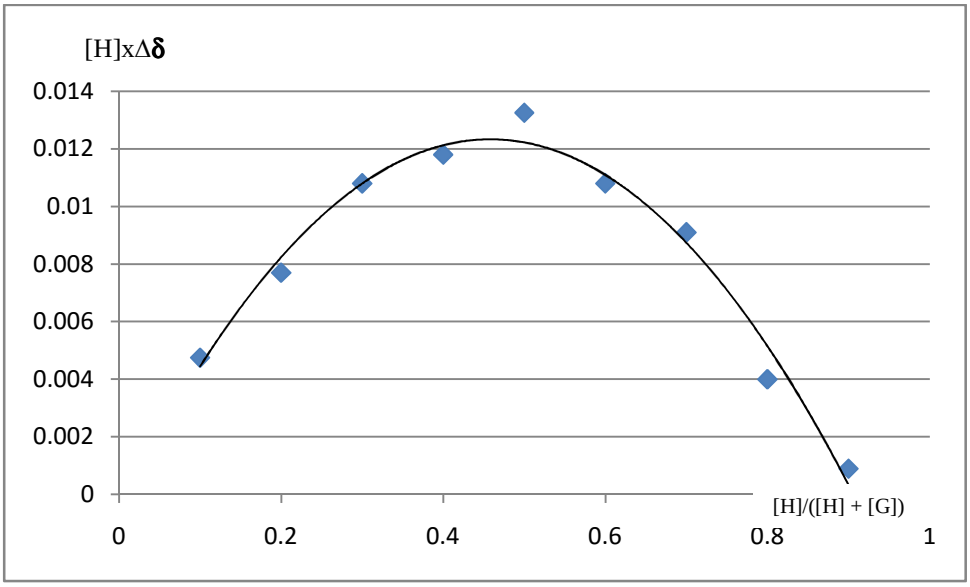


Figure S11. Job plot of **1** (5mM) with **G4** (5mM) in CD_3CN

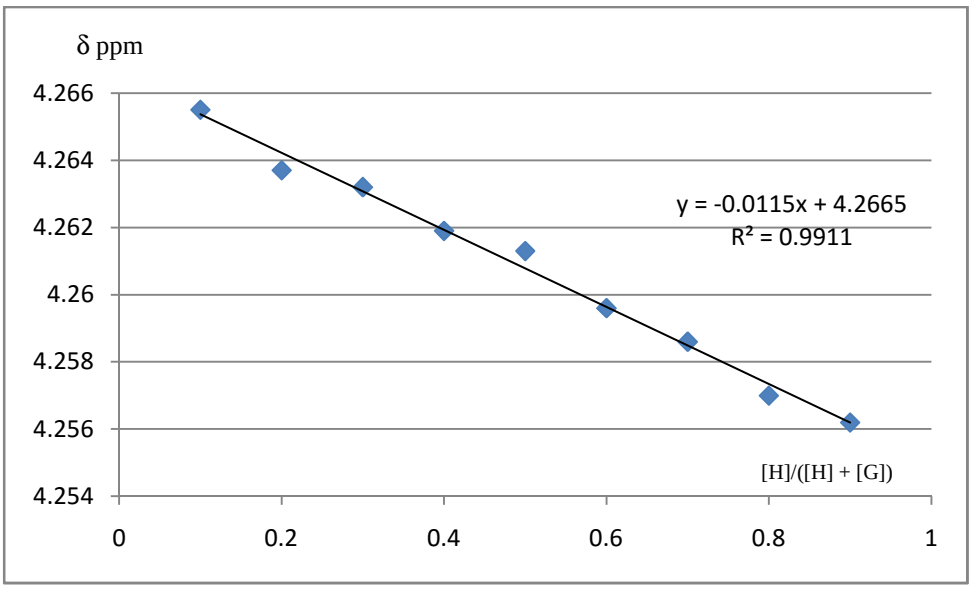


Figure S12. Determination of δ_c

The values of the association constants (Table 6) were calculated using the following equations (1 and 2):

$$\delta = \frac{[H]-x}{[H]} * \delta_H + \frac{x}{[H]} * \delta_C \quad (1)$$

$$K = \frac{x}{([G]-x)([H]-x)} \quad (2)$$

where [H] and [G] are the total concentrations of host (H) and guest (G) and x is the concentration of the formed complex, while δ, δ_H and δ_c are the experimental δ values of the test signal at different host/guest ratios (δ), the δ value of the test signal in the free host molecule (δ_H) and the δ value of the test signal in the complex (δ_c).[4]

The δ_c values were taken from the linear representations of figures S6, S8, S10 and S12 and were used in equation 1 to determine x values that introduced in equation 2 led to the K values.

Table 6.Values of the association constants for **G1**-**G4**.

Guest	δc ppm	K L/mol x 10^3			Average K value L/mol x 10^3
		[H]/[G] ratio			
		1/1.5	1/1	1.5/1	
PyxHCl (G1)	4.2665	1.94	2.20	2.46	2.20 ± 0.26
PyxHBr (G2)	4.3104	1.58	1.95	1.83	1.79 ± 0.19
TBAI (G3)	4.2823	1.78	1.56	1.70	1.68 ± 0.11
TBAHS (G4)	4.2665	1.36	1.62	1.07	1.35 ± 0.28

The values of the association constants reveal similar binding abilities of *β*-HCH for the investigated anions with a slight preference for halides over HSO_4^-. Among halide anions a decreasing of the constants' values from Cl^- to I^- is observed.

2.3.ESI(-)-HRMS spectra

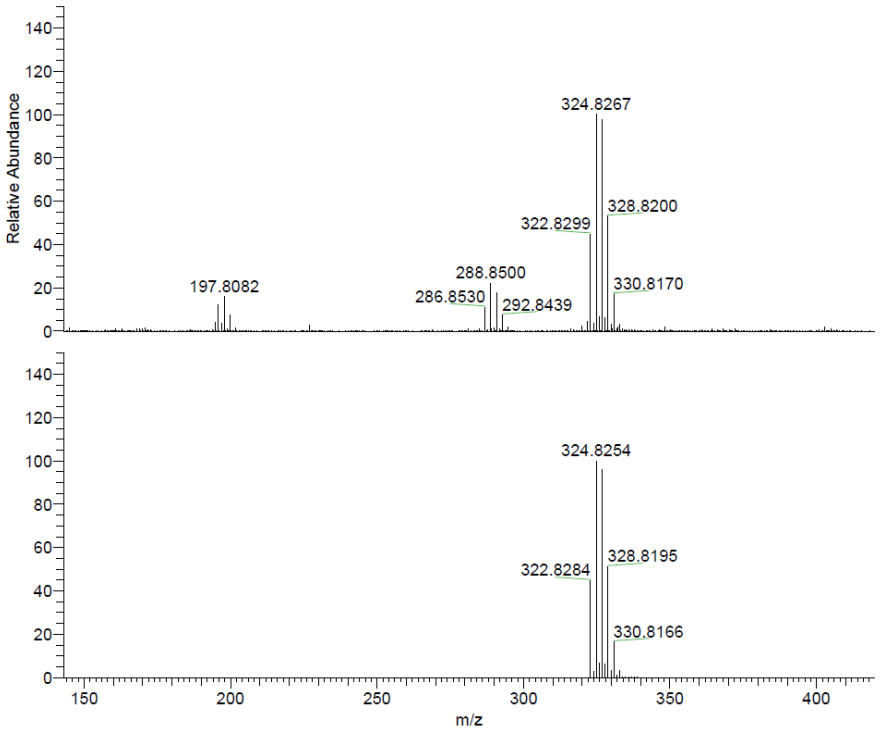


Figure S13. ESI(-)-HRMS spectra of [HCH•Cl^-] complex. Comparison of the experimental spectrum (top) and simulated isotopic pattern (bottom).

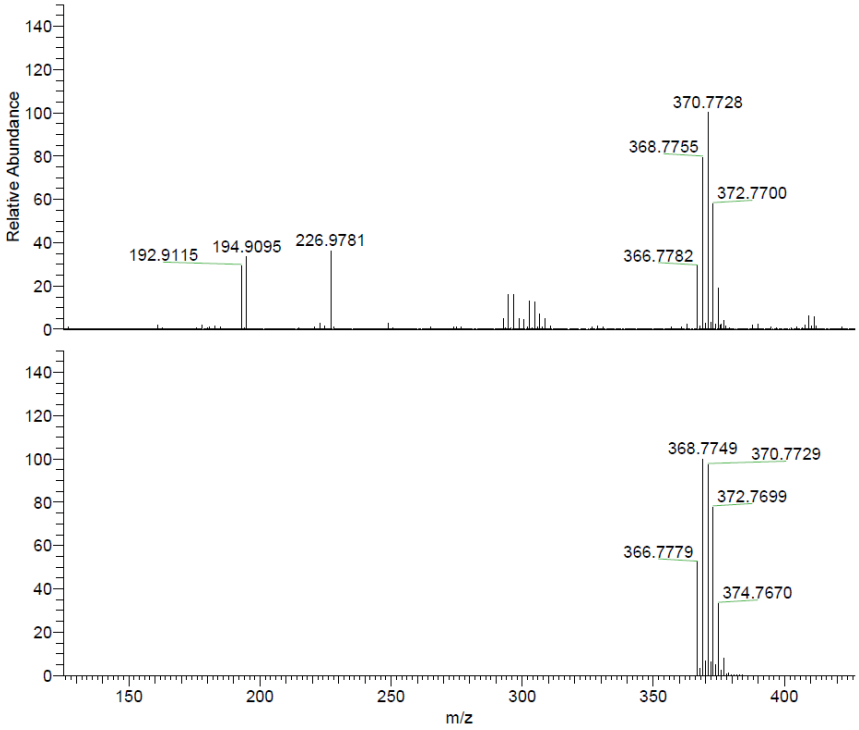


Figure S14. ESI(-)-HRMS spectrum of [HCH•Br^-] complex. Comparison of the experimental spectrum (top) and simulated isotopic pattern (bottom).

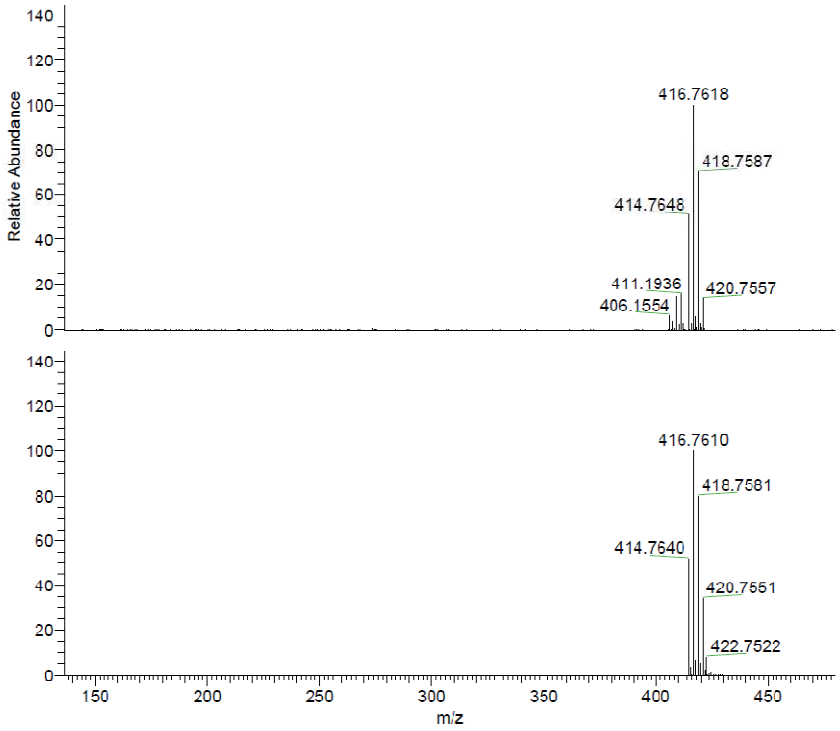


Figure S15. ESI(-)-HRMS spectra of [HCH•I$^-$] complex. Comparison of the experimental spectrum (top) and simulated isotopic pattern (bottom).

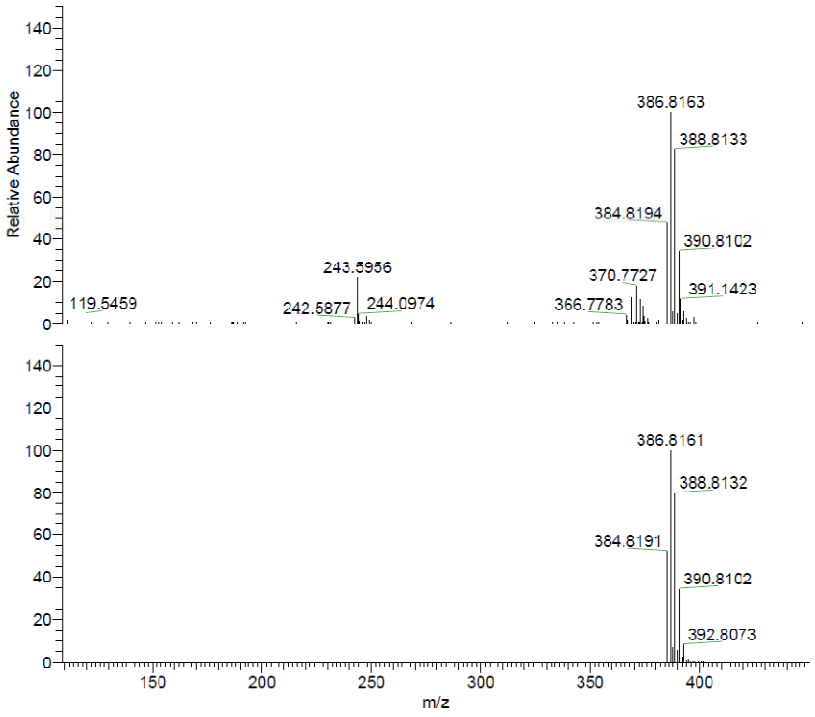


Figure S16. ESI(-)-HRMS spectra of [HCH•HSO_4^-] complex. Comparison of the experimental spectrum (top) and simulated isotopic pattern (bottom).

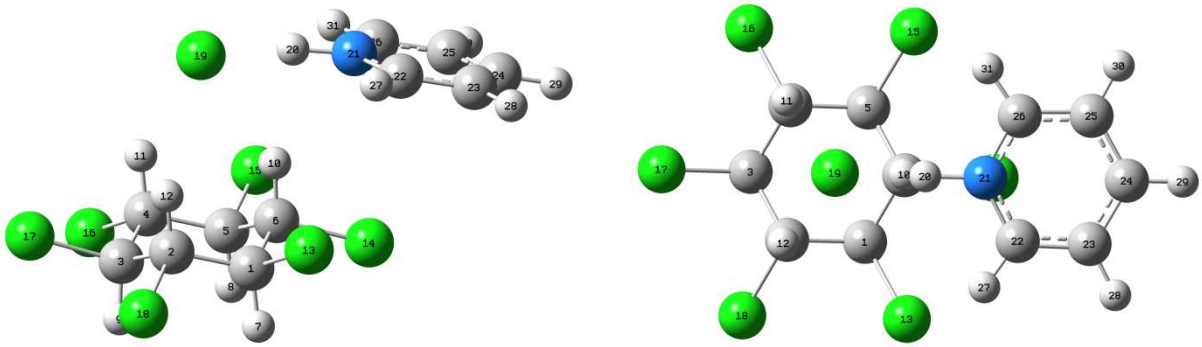
3. Theoretical calculations

3.1.Computational details

The structures, intermolecular interaction energies, and natural charge distribution analysis of all molecular complexes have been obtained with DF-LMP2[5,6] (density fitting local second order Møller-Plesset perturbation theory) method considering the aug-cc-pVTZ[7,8] basis set. For all DF-LMP2 calculations, we have used the Molpro.2012 program,[9,10] applying default thresholds and algorithms.

3.2. Geometry of structures:

A. **β-HCH ··· (Cl^- ··· H^+-Pyridine)**



(a) (b)

Figure S1. The geometry configuration of β-HCH ··· (Cl^- ··· H^+-Pyridine) complex. (a) side view and (b) top view.

Distances:

Cl^-(19) ··· H(10) = 2.522Å; Cl^-(19) ··· H(11) = 2.758 Å; Cl^-(19) ··· H(12) = 2.750Å;

Cl^-(19) ··· H^+(20) = 1.700 Å;

H^+(20) – N(21) = 1.144 Å;

Effective natural charges (NPA):

q[Cl^-(19)] = -0.75*e*; *q*[β-HCH] = -0.02*e*; *q*[H^+-Pyridine] = +0.77*e* and *q*[Pyridine] = +0.33*e*;

The intermolecular interaction energy between the β-HCH and Cl^- ··· H^+-Pyridine complex are -4.735 kcal/mol, -17.056kcal/mol and -16.499 kcal/mol calculated at HF/aug-cc-pVTZ, DF-LMP2/aug-cc-pVTZ and DF-LCCSD(T)/aug-cc-pVTZ levels of theory, respectively.

Cartesian coordinates:

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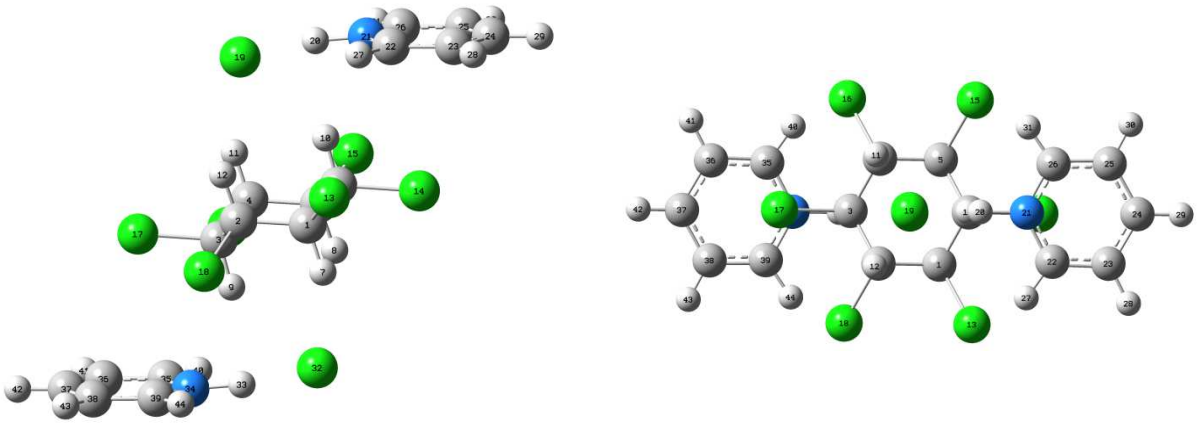
C	0.3436739936	1.5227891969	-0.4183215309
C	1.3612806020	0.4238951601	-0.1043385716
C	0.8800866867	-0.9316446606	-0.6285451287
C	-0.5029373210	-1.2851525319	-0.0751836365
C	-1.5144463158	-0.1825951716	-0.3960292667
C	-1.0308763094	1.1625716504	0.1406231016
H	0.2892924312	1.6964498170	-1.4953011176
H	-1.6925274375	-0.1290776550	-1.4723584824
H	0.8544313220	-0.9229346422	-1.7208847807
H	-0.9672206541	1.1062931037	1.2259045196
H	-0.4472652653	-1.4367345592	1.0048608939
H	1.5304804204	0.3702881706	0.9731372785
Cl	0.8926435543	3.0623531547	0.3151591855
Cl	-2.2099883907	2.4439131528	-0.2829435488
Cl	-3.0882956197	-0.5860357022	0.3584337578
Cl	-1.0581934816	-2.8127319859	-0.8199984077
Cl	2.0468000167	-2.1949515036	-0.1512251403
Cl	2.9146481186	0.8360799114	-0.8883702169
Cl	0.0687988922	0.0508980920	3.2693543930
H	-1.0588663823	1.3162396169	3.3905262273
N	-1.8322735940	2.1552754430	3.3098240747
C	-1.4076393618	3.4212245958	3.2002245552
C	-2.3221080594	4.4449636748	2.9929712473
C	-3.6767034278	4.1316094458	2.8943511901
C	-4.0839049680	2.8028814882	3.0011168998
C	-3.1256248367	1.8201959313	3.2086315227
H	-0.3383461211	3.5680332343	3.2690130949
H	-1.9726145093	5.4636130785	2.9018304284
H	-4.4057089422	4.9129875943	2.7248914749
H	-5.1248434756	2.5250344877	2.9156821171
H	-3.3455315646	0.7637084120	3.2825638665

B. **β-HCH ··· 2x(Cl^- ··· H^+-Pyridine)**



(a) (b)

Figure S2. The geometry configuration of β-HCH ··· 2x(Cl^- ··· H^+-Pyridine) complex.(a) side view and (b) top view.

Distances:

Cl^-(19) ··· H(10) = 2.588Å; Cl^-(19) ··· H(11) = 2.745 Å; Cl^-(19) ··· H(12) = 2.745Å;

Cl^-(19) ··· H^+(20) = 1.709 Å;

H^+(20) – N(21) = 1.138 Å;

Cl^-(32) ··· H(9) = 2.588Å; Cl^-(32) ··· H(8) = 2.745 Å; Cl^-(32) ··· H(7) = 2.745Å;

Cl^-(32) ··· H^+(33) = 1.709 Å;

H^+(33) – N(34) = 1.139 Å;

Effective natural charges (NPA):

q[Cl^-(19) and Cl^-(32)] = -0.75*e*; *q*[β-HCH] = -0.02*e*; *q*[H^+-Pyridine] = +0.77*e* and *q*[Pyridine] = +0.33*e*;

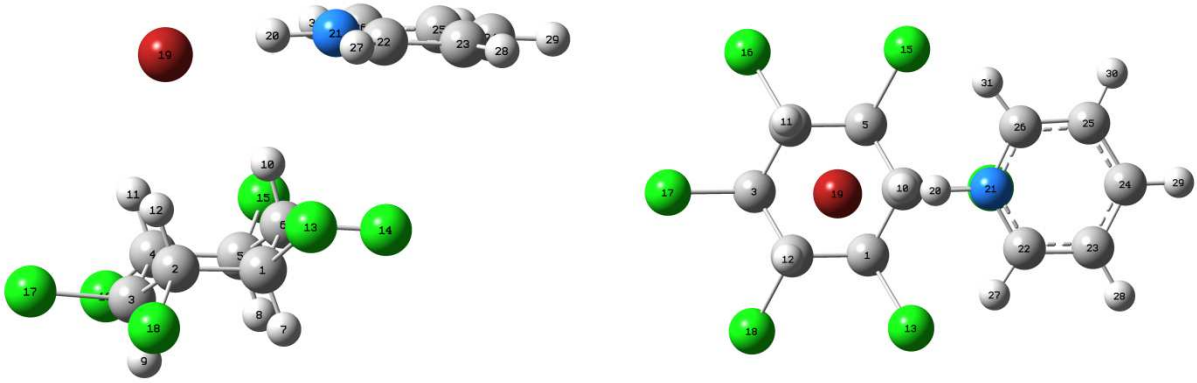
The intermolecular interaction energy between the β-HCH and 2x(Cl^- ··· H^+-Pyridine) complex are -8.529 kcal/mol, -33.638 kcal/mol and -32.550 kcal/mol calculated at HF/aug-cc-pVTZ, DF-LMP2/aug-cc-pVTZ and DF-LCCSD(T)/aug-cc-pVTZ levels of theory, respectively.

Cartesian coordinates:

44

C	0.44468	1.52578	-0.54579
C	1.46345	0.42933	-0.22655
C	0.98818	-0.90857	-0.79206
C	-0.38495	-1.29218	-0.24159
C	-1.40336	-0.19567	-0.56190
C	-0.92862	1.14216	0.00402
H	0.39553	1.70097	-1.62262
H	-1.56393	-0.12528	-1.63983
H	0.92574	-0.83265	-1.87600
H	-0.86757	1.06626	1.08797
H	-0.33593	-1.46667	0.83532
H	1.62529	0.35896	0.85114
Cl	0.97838	3.05609	0.22561
Cl	-2.11799	2.42303	-0.38855
Cl	-2.97522	-0.62564	0.19042
Cl	-0.91860	-2.82293	-1.01161
Cl	2.17801	-2.18914	-0.40009
Cl	3.03454	0.85984	-0.97981
Cl	0.19292	-0.08213	3.15058
H	-0.96578	1.16870	3.26369
N	-1.74051	1.99936	3.18380
C	-1.31776	3.26692	3.08696
C	-2.23360	4.29033	2.88530
C	-3.58692	3.97496	2.77837
C	-3.99133	2.64436	2.86926
C	-3.03208	1.66163	3.07139
H	-0.24892	3.41448	3.15945
H	-1.88543	5.31001	2.80177
H	-4.31680	4.75603	2.61116
H	-5.03074	2.36455	2.77294
H	-3.24974	0.60405	3.13198
Cl	-0.13020	0.32161	-3.93783
H	1.04152	-0.91642	-4.05078
N	1.81738	-1.74662	-3.97207
C	1.39152	-3.01317	-3.87521
C	2.30481	-4.03912	-3.67496
C	3.65900	-3.72726	-3.56901
C	4.06668	-2.39759	-3.65932
C	3.10983	-1.41222	-3.86008
H	0.32212	-3.15762	-3.94654
H	1.95405	-5.05794	-3.59176
H	4.38718	-4.51035	-3.40395
H	5.10693	-2.12058	-3.56394
H	3.33056	-0.35530	-3.92026

C. **β-HCH ⋯ (Br⁻ ⋯ H⁺-Pyridine)**



(a) (b)

Figure S3. The geometry configuration of β-HCH ⋯ (Br⁻ ⋯ H⁺-Pyridine) complex. (a) side view and (b) top view.

Distances:

Br⁻(19) ⋯ H(10) = 2.660 Å;Br⁻(19) ⋯ H(11) = 2.958 Å; Br⁻(19) ⋯ H(12) =2.866 Å;

Br⁻(19) ⋯ H⁺(20) = 1.908 Å;

H⁺(20) – N(21) = 1.111 Å;

Effective natural charges (NPA):

q[Br⁻(19)] = -0.77*e*; *q*[β-HCH] = -0.02*e*; *q*[H⁺-Pyridine] = +0.79*e* and *q*[Pyridine] = +0.35*e*;

The intermolecular interaction energy between the β-HCH and Br⁻ ⋯ H⁺-Pyridine complex are -4.249 kcal/mol, -17.308 kcal/mol and -16.712 kcal/mol calculated at HF/aug-cc-pVTZ, DF-LMP2/aug-cc-pVTZ and DF-LCCSD(T)/aug-cc-pVTZ levels of theory, respectively.

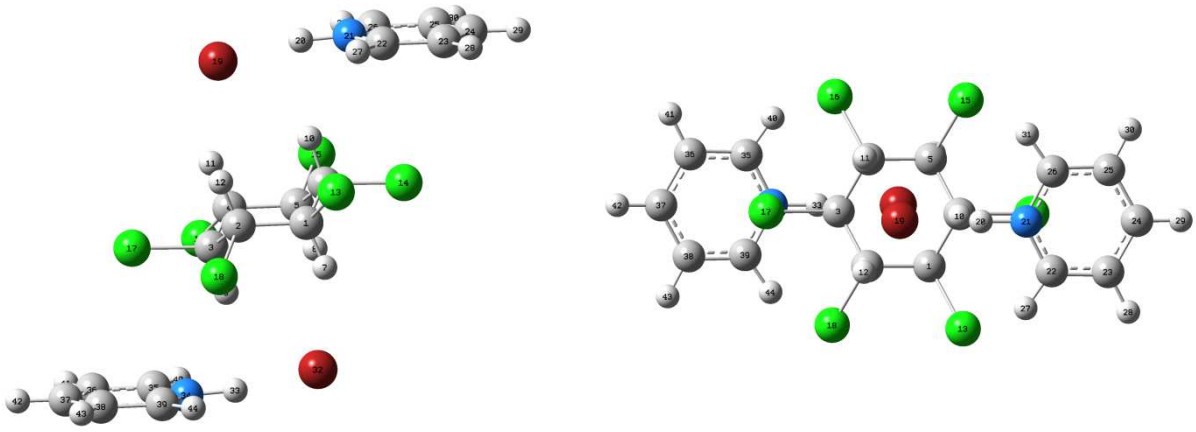
Cartesian coordinates:

31

C	0.3607456585	1.5118969043	-0.3910304749
C	1.3761924963	0.3954795582	-0.1374338431
C	0.8751097562	-0.9381264811	-0.6973247330
C	-0.4959267925	-1.2998305424	-0.1202561763
C	-1.5079134424	-0.1832523885	-0.3857429144
C	-1.0039431760	1.1400750472	0.1838452039

H	0.2848351550	1.7219011250	-1.4602345979
H	-1.7070555506	-0.0951735444	-1.4561350412
H	0.8230461832	-0.8924606433	-1.7877250305
H	-0.9191857163	1.0472292332	1.2667500510
H	-0.4155885389	-1.4785282280	0.9552938268
H	1.5657115455	0.3003698346	0.9340383759
Cl	0.9347010197	3.0218537058	0.3829604710
Cl	-2.1828257337	2.4411215846	-0.1800073686
Cl	-3.0677617948	-0.5991602763	0.3908641135
Cl	-1.0804369451	-2.8031463739	-0.8900240967
Cl	2.0438107647	-2.2230835248	-0.2897661060
Cl	2.9166820242	0.8272054616	-0.9353432451
Br	0.2053187056	0.0021298444	3.4387626983
H	-1.1032197347	1.3912158204	3.4785860984
N	-1.8608859289	2.1929174676	3.3471983527
C	-1.4352595858	3.4552454862	3.2069424888
C	-2.3529326609	4.4664731664	2.9598650498
C	-3.7044787118	4.1420020888	2.8540415068
C	-4.1075641035	2.8145351383	2.9908240673
C	-3.1489367648	1.8418296030	3.2375689532
H	-0.3672611496	3.6044506978	3.2883488093
H	-2.0079868271	5.4840863225	2.8444422474
H	-4.4355828422	4.9144956346	2.6552901507
H	-5.1460560808	2.5298783584	2.8993635802
H	-3.3591312284	0.7858099193	3.3416375828

D. **β-HCH ··· 2x(Cl⁻ ··· H⁺-Pyridine)**



(a) (b)

Figure S4. The geometry configuration of β-HCH ··· 2x(Br⁻ ··· H⁺-Pyridine) complex. (a) Side view and (b) top view.

Distances:

Br^-(19) ··· H(10) = 2.733 Å;Br^-(19) ··· H(11) = 2.880 Å; Br^-(19) ··· H(12) = 2.876 Å;

Br^-(19) ··· H^+(20) = 1.922 Å;

H^+(20) – N(21) = 1.106 Å;

Br^-(32) ··· H(9) = 2.733 Å;Br^-(32) ··· H(8) = 2.878 Å; Br^-(32) ··· H(7) = 2877 Å;

Br^-(32) ··· H^+(33) = 1.922 Å;

H^+(33) – N(34) = 1.106 Å;

Effective natural charges (NPA):

q[Br^-(19) and Br^-(32)] = -0.78*e*; *q*[β-HCH] = -0.04*e*; *q*[H^+-Pyridine] = +0.80*e* and *q*[Pyridine] = +0.35*e*;

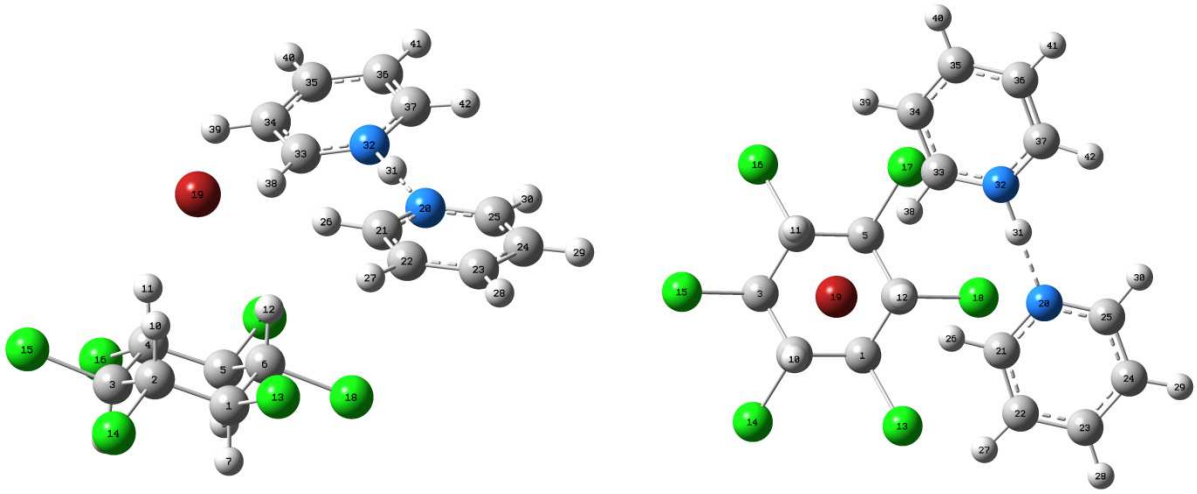
The intermolecular interaction energy between the β-HCH and 2x(Br^- ··· H^+-Pyridine) complex are -7.148 kcal/mol and -34.050 kcal/mol calculated at HF/aug-cc-pVTZ and DF-LMP2/aug-cc-pVTZ levels of theory, respectively.

Cartesian coordinates:

44

C	0.4424008798	1.5311706546	-0.5184363319
C	1.4683606633	0.4271587685	-0.2534500067
C	0.9804922956	-0.8994962049	-0.8342362533
C	-0.3824717063	-1.2967921339	-0.2687016910
C	-1.4084689107	-0.1928793537	-0.5347070758
C	-0.9209080613	1.1337872014	0.0463048579
H	0.3716191340	1.7393087065	-1.5884287435
H	-1.6004258465	-0.0986152895	-1.6059139504
H	0.9022643754	-0.8067146256	-1.9170189894
H	-0.8440602102	1.0406631018	1.1291341742
H	-0.3116812975	-1.5041561979	0.8014406530
H	1.6612443525	0.3325449582	0.8175589505
Cl	0.9916069031	3.0382888098	0.2871794816
Cl	-2.1159133896	2.4206261718	-0.3129354988
Cl	-2.9585319087	-0.6403301175	0.2520782185
Cl	-0.9314049788	-2.8044118576	-1.0734717898
Cl	2.1763127462	-2.1857754936	-0.4758587719
Cl	3.0179279019	0.8751449704	-1.0410649101
Br	0.2899519886	-0.1879006970	3.2912471188
H	-1.0145378174	1.2221327637	3.3602241466
N	-1.7644993288	2.0255072063	3.2334716833
C	-1.3343712468	3.2887822958	3.1158993528
C	-2.2474109630	4.3051127051	2.8730407255
C	-3.5982707762	3.9855083652	2.7477782244
C	-4.0052728870	2.6571520808	2.8592199184
C	-3.0518609424	1.6786932731	3.1024081584
H	-0.2667998109	3.4339098694	3.2078455721
H	-1.8984320040	5.3228913296	2.7727034853
H	-4.3248492056	4.7622450602	2.5491647588
H	-5.0425039160	2.3752381377	2.7478743717
H	-3.2658747553	0.6218816980	3.1840297581
Br	-0.2271134374	0.4274172722	-4.0786802950
H	1.0932151653	-0.9677241766	-4.1463143290
N	1.8427347250	-1.7717696995	-4.0213480510
C	1.4076493342	-3.0335228049	-3.9054382680
C	2.3165706541	-4.0539363557	-3.6643676095
C	3.6686890878	-3.7398780269	-3.5389811809
C	4.0809381355	-2.4129587815	-3.6486211236
C	3.1314804947	-1.4302328695	-3.8901867621
H	0.3393480293	-3.1738402962	-3.9970330242
H	1.9634552676	-5.0704064091	-3.5652844741
H	4.3922912392	-4.5197141991	-3.3416507495
H	5.1193544943	-2.1354505389	-3.5372179839
H	3.3500755329	-0.3742992710	-3.9702357463

E. **β-HCH ⋯ (Br⁻ ⋯Pyridine-H$^+$ ⋯ Pyridine)**



(a) (b)

Figure S5. The geometry configuration of β-HCH ⋯ (Br⁻ ⋯Pyridine-H$^+$ ⋯Pyridine) complex. (a) side view and (b) top view.

Distances:

Br⁻(19) ⋯ H(10) = 2.674 Å;Br⁻(19) ⋯ H(11) = 2.737 Å; Br⁻(19) ⋯ H(12) = 2767 Å;

Br⁻(19) ⋯ H$^+$(31) = 4.053 Å;

H$^+$(31) – N(32) = 1.090 Å;H$^+$(31) ⋯ N(20) = 1.616 Å

Effective natural charges (NPA):

q[Br⁻(19)] = -0.91*e*; *q*[β-HCH] = -0.03*e*; *q*[H$^+$-Pyridine1] = +0.86*e*; *q*[Pyridine1] = +0.36*e*and *q*[Pyridine2] = +0.08*e*;

The intermolecular interaction energy between the β-HCH and Br⁻ ⋯ Pyridine-H$^+$ ⋯Pyridine complex are -5.916 kcal/mol and -20.609 kcal/mol calculated at HF/aug-cc-pVTZ and DF-LMP2/aug-cc-pVTZ levels of theory, respectively.

Cartesian coordinates:

42

C	0.1481980000	1.9505710000	12.9442780000
C	0.6072450000	1.9227420000	14.4036340000
C	0.1707650000	3.2034980000	15.1204090000

C	0.6819420000	4.4544530000	14.4014020000
C	0.2494630000	4.4575770000	12.9334880000
C	0.7021260000	3.1813530000	12.2247860000
H	-0.9441330000	1.9430010000	12.8928510000
H	-0.9194770000	3.2344370000	15.1879600000
H	-0.8330290000	4.5774290000	12.8538360000
H	1.6908560000	1.8050250000	14.4528600000
H	1.7735190000	4.5060380000	14.4681900000
H	1.7914650000	3.1365610000	12.2096260000
Cl	0.7089700000	0.4692950000	12.1148120000
Cl	-0.1509240000	0.5215490000	15.2204610000
Cl	0.7880300000	3.1923950000	16.7957220000
Cl	0.0035340000	5.9049860000	15.2031000000
Cl	0.9633550000	5.8838950000	12.1095730000
Cl	0.1165910000	3.1985010000	10.5321360000
Br	4.0062030000	3.0604830000	13.7066820000
N	3.9364860000	3.0071190000	9.3343540000
C	3.7054180000	2.0016310000	10.2019590000
C	3.4304260000	0.7057730000	9.7727350000
C	3.3899630000	0.4327030000	8.4087640000
C	3.6218670000	1.4739740000	7.5117150000
C	3.8883210000	2.7424340000	8.0152270000
H	3.7698140000	2.2377680000	11.2623930000
H	3.2531780000	-0.0653190000	10.5092150000
H	3.1808210000	-0.5668800000	8.0502190000
H	3.5969460000	1.3131410000	6.4422340000
H	4.0651890000	3.5785710000	7.3477700000
H	4.3005250000	4.4695420000	9.9175300000
N	4.5483500000	5.4536030000	10.3165430000
C	4.2608290000	5.7024880000	11.6029760000
C	4.5588260000	6.9506410000	12.1378000000
C	5.1449020000	7.9204070000	11.3292740000
C	5.4293540000	7.6225960000	9.9947130000
C	5.1152130000	6.3649360000	9.5062680000
H	3.8516650000	4.8798690000	12.1901880000
H	4.3297820000	7.1373270000	13.1775820000
H	5.3841920000	8.8964760000	11.7307200000
H	5.8876810000	8.3501660000	9.3403040000
H	5.2972800000	6.0571330000	8.4862520000

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