Theoretical Insights into the Stability and Nature of Nonconventional C–H···Y (Y = N, P, As, Sb) Hydrogen Bonds in Haloform–Pnictogen Trihydride Complexes

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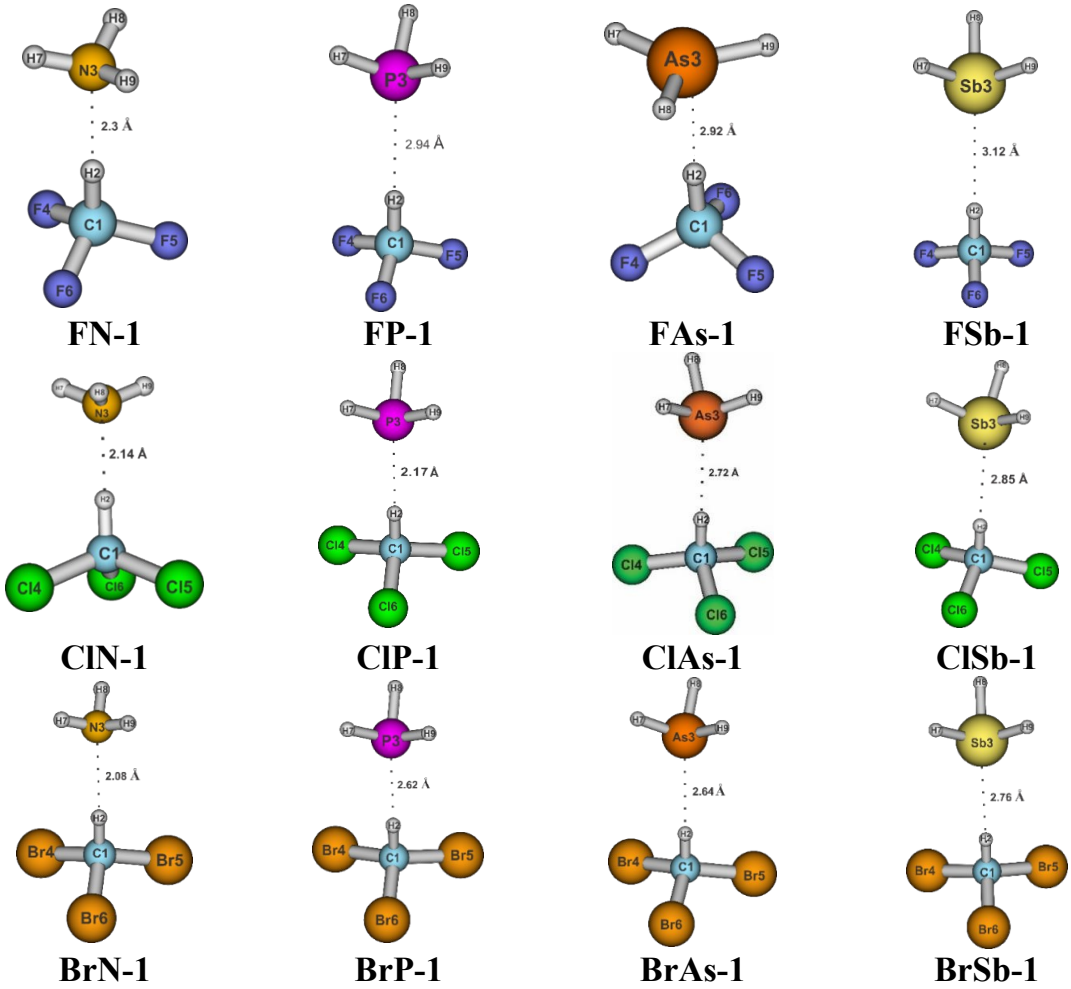
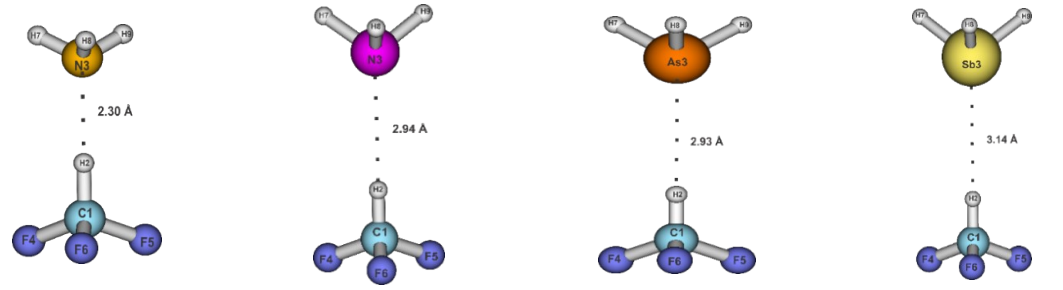
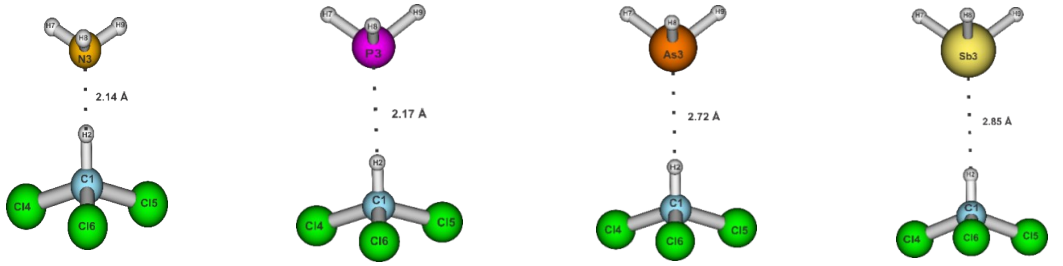


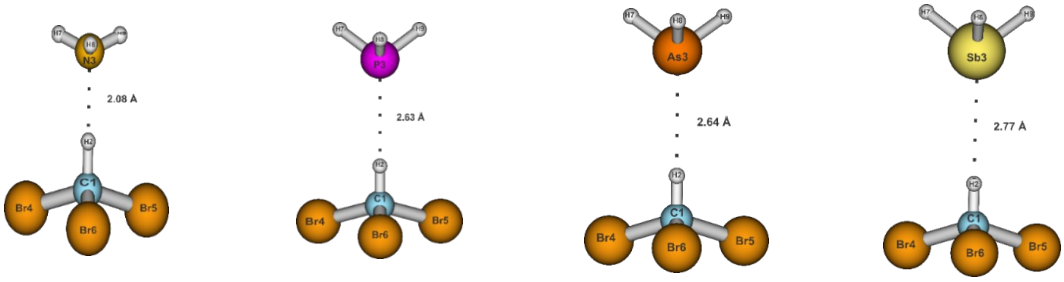
Figure S1a: Stable structures of XY-1 complexes (X= F, Cl, Br; Y= N, P, As, Sb)



FN-2 **FP-2** **FAs-2** **FSb-2**



ClN-2 **ClP-2** **ClAs-2** **ClSb-2**



BrN-2 **BrP-2** **BrAs-2** **BrSb-2**

Figure S1b: Stable structures of XY-2 complexes (X= F, Cl, Br; Y= N, P, As, Sb)

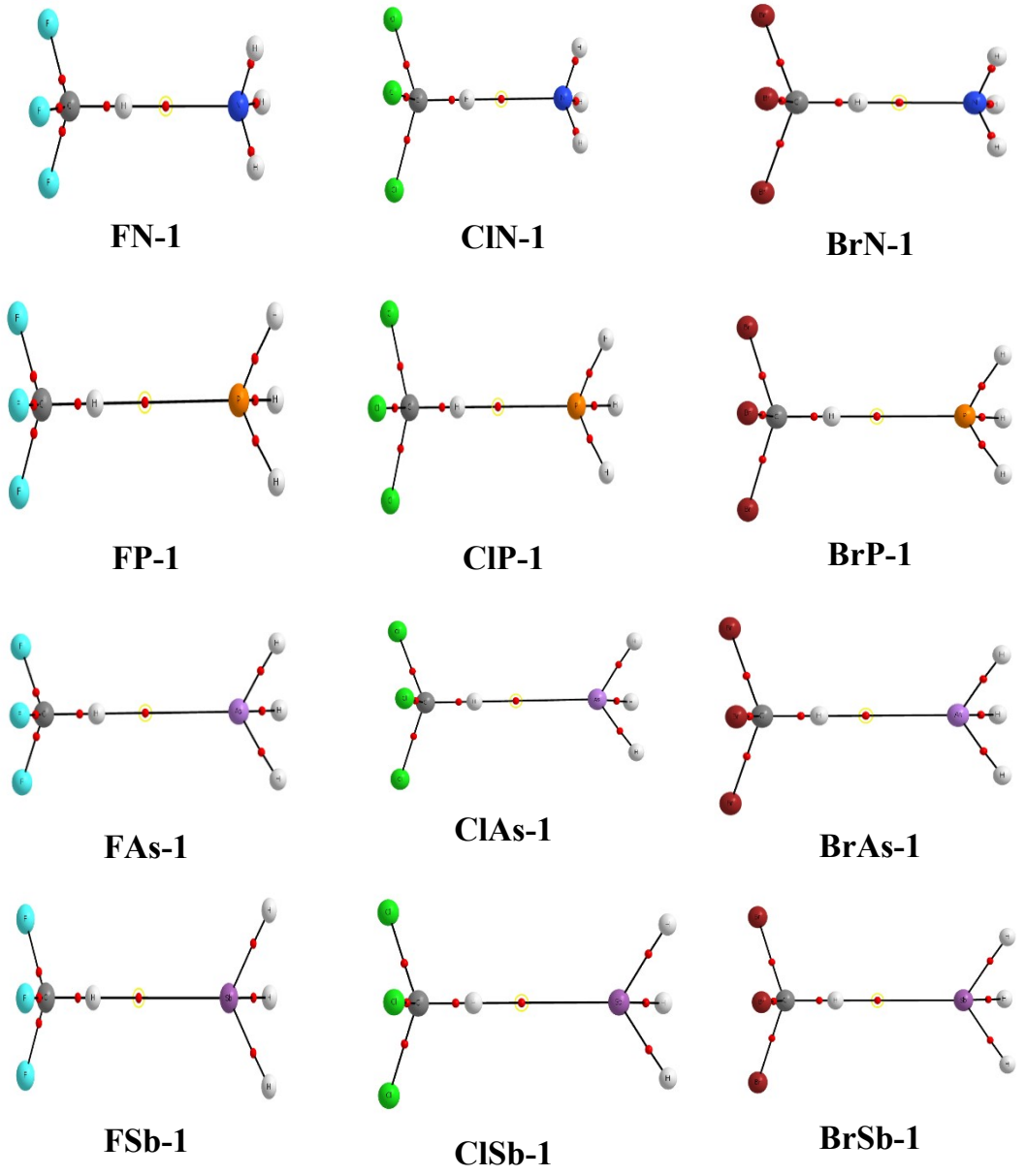


Figure S2a: Topological structures of XY-1 complexes (X= F, Cl, Br; Y= N, P, As, Sb)

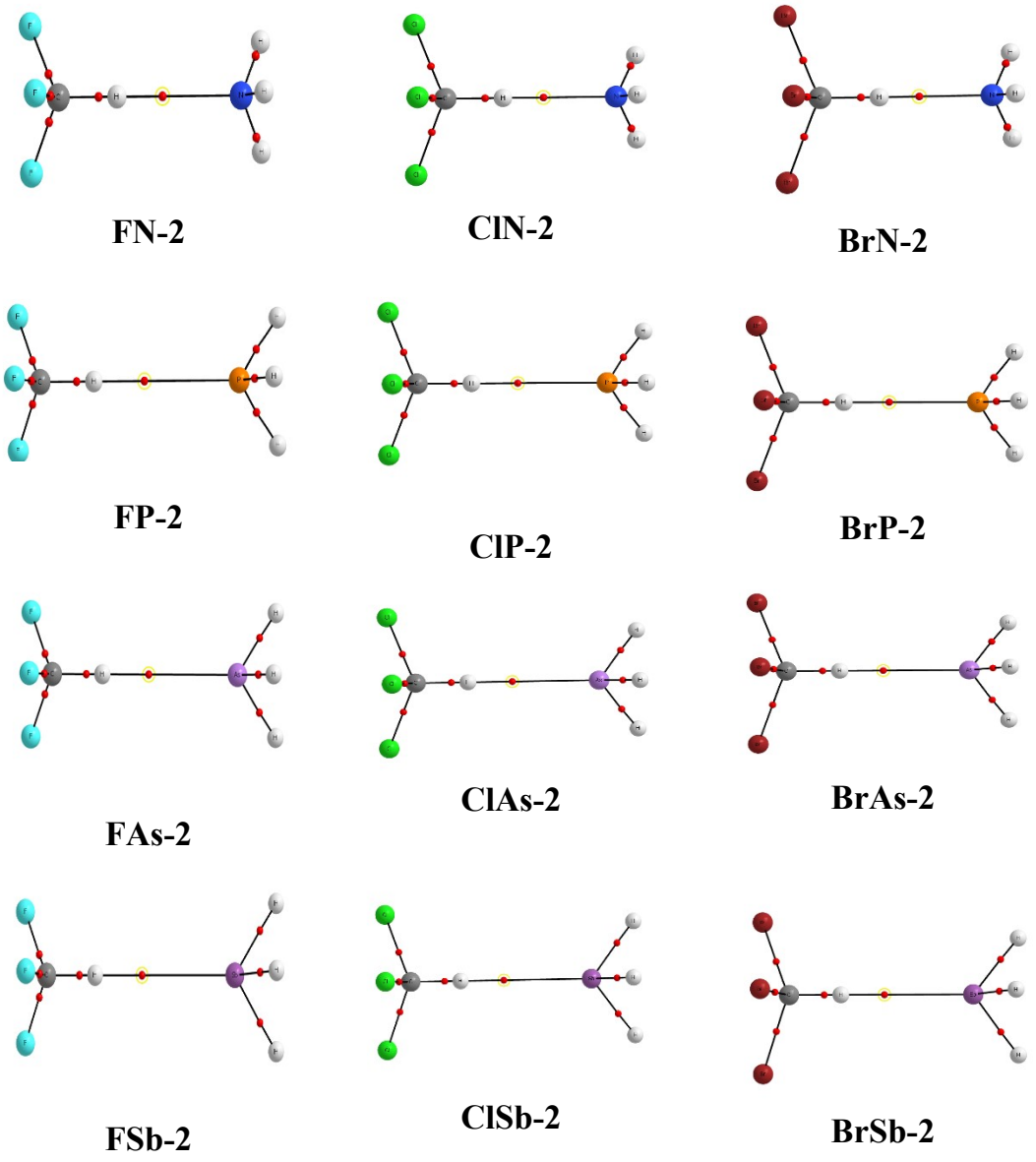


Figure S2b: Topological structures of XY-2 complexes (X= F, Cl, Br; Y= N, P, As, Sb)

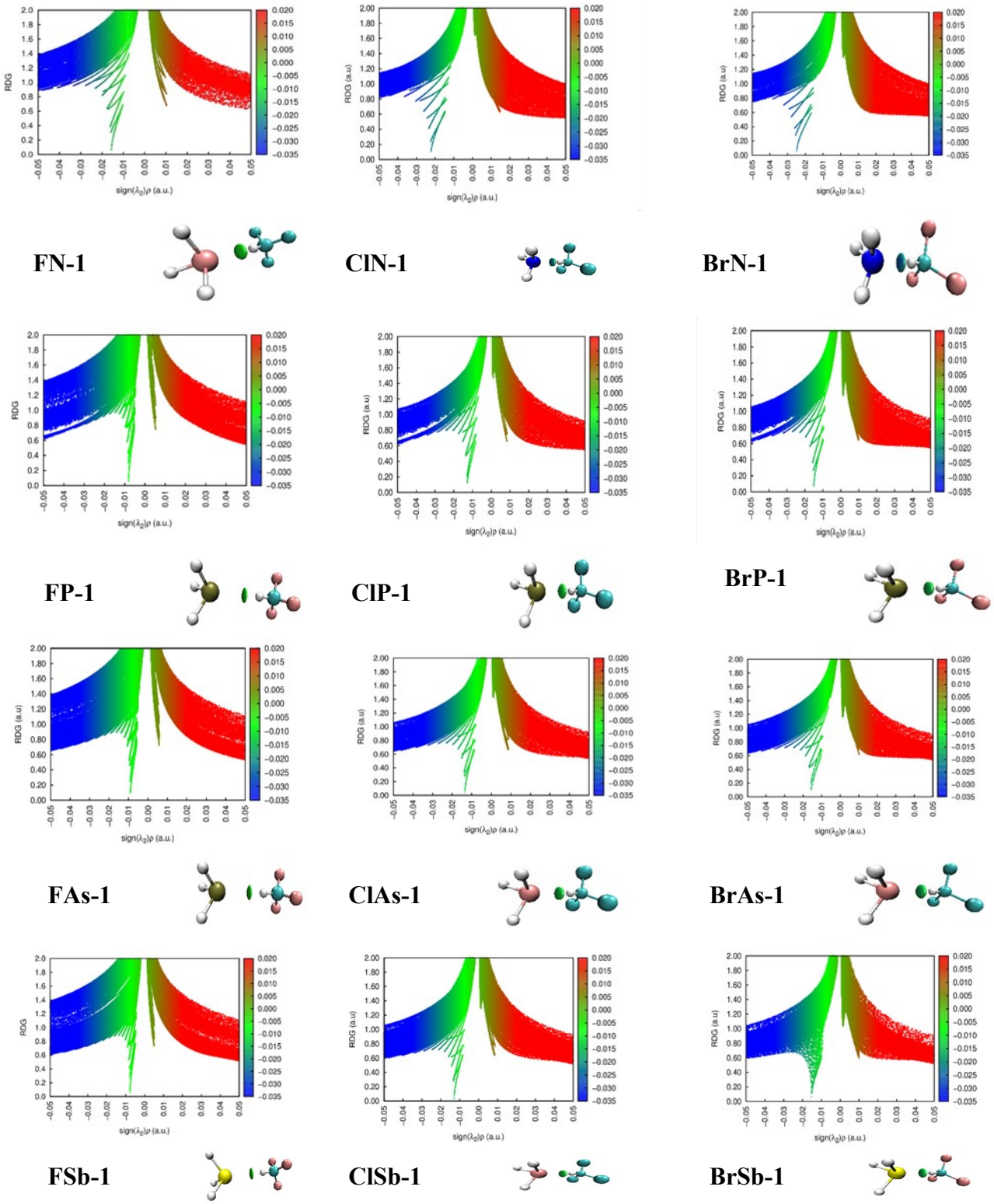


Figure S3a. The 2D diagrams and isosurfaces obtained from NCIplot for XY-1 complexes (X = F, Cl, Br; Y = N, P, As, Sb)

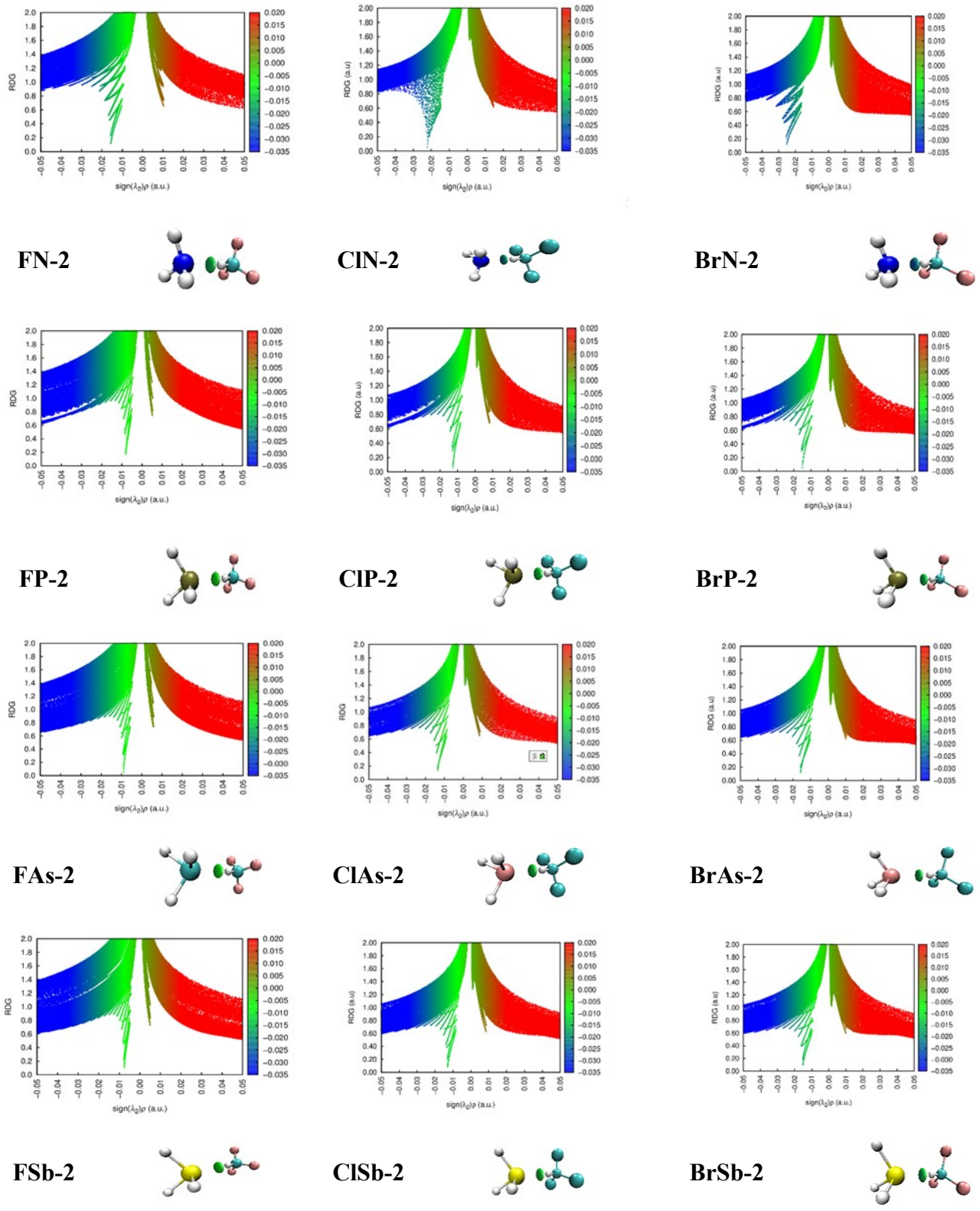


Figure S3b. The 2D diagrams and isosurfaces obtained from NCIplot for XY-2 complexes (X = F, Cl, Br; Y = N, P, As, Sb)

Table S1. Contribution of different energy components to the total interaction energy calculated

using SAPT2+. All energy components and the total SAPT2+ interaction energy are given in kJ.mol^{-1}.

Complex	E_{elst}	E_{disp}	E_{ind}	δE_{HF}	E_{exch}	E_{SAPT2+}	%elst	%disp	%ind	$\%\delta E_{HF}$
FN-1	-28.8	-9.2	-9.4	-3.0	30.0	-20.4	57.1	18.3	18.6	6.0
FP-1	-10.1	-6.5	-5.3	-1.5	15.5	-7.8	43.1	27.9	22.6	6.4
FAs-1	-10.1	-7.6	-7.0	-1.9	20.1	-6.4	38.0	28.5	26.4	7.1
FSb-1	-6.3	-7.2	-6.3	-1.7	17.7	-3.8	29.2	33.6	29.3	7.9
ClN-1	-37.3	-15.8	-17.4	-5.7	50.5	-25.8	48.9	20.8	22.8	7.4
ClP-1	-14.9	-13.0	-10.3	-3.1	31.1	-10.2	36.1	31.5	24.9	7.5
ClAs-1	-14.5	-14.4	-13.4	-3.8	37.5	-8.7	31.5	31.2	29.1	8.2
ClSb-1	-11.6	-15.4	-12.9	-3.7	39.1	-4.6	26.6	35.4	29.5	8.6
BrN-1	-41.2	-18.7	-21.3	-6.7	60.7	-27.2	46.8	21.2	24.3	7.7
BrP-1	-17.4	-16.3	-14.1	-4.2	41.0	-11.1	33.4	31.3	27.2	8.1
BrAs-1	-19.7	-17.8	-18.8	-2.1	48.6	-9.3	34.1	30.7	31.5	3.7
BrSb-1	-14.3	-19.4	-18.2	-4.7	51.9	-4.7	25.3	34.2	32.1	8.3
FN-2	-28.8	-9.2	-9.4	-3.0	30.0	-20.5	57.1	18.3	18.6	6.0
FP-2	-10.0	-6.5	-5.2	-1.5	15.4	-7.8	43.1	27.9	22.6	6.4
FAs-2	-10.0	-7.6	-7.0	-1.9	20.0	-6.4	37.8	28.6	26.4	7.2
FSb-2	-6.2	-7.2	-6.2	-1.7	17.4	3.8	29.2	33.7	29.3	7.9
ClN-2	-37.5	-15.9	-17.5	-5.7	50.6	-25.9	49.0	20.8	22.9	7.4
ClP-2	-14.8	-13.0	-10.2	-3.1	30.8	-10.2	36.0	31.6	24.8	7.5
ClAs-2	-14.5	-14.4	-13.4	-3.7	37.4	-8.6	31.5	31.3	29.1	8.1
ClSb-2	-11.5	-15.4	-12.8	-3.7	38.9	-4.5	26.5	35.4	29.5	8.6
BrN-2	-41.6	-18.9	-21.7	-7.0	61.8	-27.4	46.6	21.2	24.3	7.9
BrP-2	-17.3	-16.3	-14.0	-4.1	40.7	11.0	33.5	31.5	27.1	8.0
BrAs-2	-19.5	-17.9	-18.8	-2.3	48.7	-9.2	33.7	30.8	31.5	3.9
BrSb-2	-14.1	-19.3	-17.9	-4.6	51.3	-4.7	25.2	34.4	32.1	8.3

Table S2. Changes in strength of the individual hydrogen bonds (E_{HB}, in kJ.mol^{-1}) in the $CHCl_3\cdots YH_3$ (Y = N, P, As, Sb) complexes as a function of the C$\cdots$Y separation.

Distance C$\cdots$Y	E_{HB} (kJ.mol^{-1})			
	C-H$\cdots$N	C-H$\cdots$P	C-H$\cdots$As	C-H$\cdots$Sb
2.8	-72.0	-99.2	-106.2	-199.3
3.0	-39.1	-60.3	-63.5	-76.2
3.2	-21.1	-36.6	-38.1	-46.0
3.4	-11.8	-22.2	-23.3	-28.0
3.6	-6.9	-13.5	-14.4	-17.3
3.8	-4.2	-8.3	-9.0	-10.9
4.0	-2.7	-5.1	-5.6	-6.9
4.2	-1.7	-3.2	-3.6	-4.5
4.4	-1.1	-2.0	-2.2	-2.9
4.6	-0.7	-1.2	-1.4	-1.9
4.8	-0.4	-0.8	-0.9	-1.2
5.0	-0.2	-0.5	-0.5	-0.8

Table S3. Changes in the C–H bond length (Δr, mÅ) and stretching frequency (Δν, cm^{-1}) in the $CH_3Cl\cdots YH_3$ (Y = N, P, As, and Sb) complexes as a function of the C⋯Y separation.

Distance C···Y	Δr(C-H) (mÅ)				Δν(C-H) (cm^{-1})			
	NH_3	PH_3	AsH_3	SbH_3	NH_3	PH_3	AsH_3	SbH_3
2.8	0.4	-37.1	-45.1	-66.5	-111.4	295.2	410.3	734.9
3.0	4.3	-19.8	-24.7	-36.9	-100.2	129.7	192.6	350.2
3.2	5.4	-9.1	-11.7	-19.0	-82.3	46.1	76.7	147.3
3.4	5.4	-2.6	-3.8	-8.2	-66.4	0.3	11.2	44.7
3.6	4.9	0.3	-0.3	-1.8	-54.4	-15.9	-11.9	-6.1
3.8	4.2	1.6	1.6	1.0	-43.6	-22.3	-22.1	-25.3
4.0	3.4	1.6	1.6	1.9	-33.8	-19.1	-19.3	-29.9
4.2	2.7	2.2	2.7	2.4	-25.6	-23.0	-29.1	-31.5
4.4	2.1	2.0	2.6	2.3	-19.3	-20.9	-27.7	-27.8
4.6	1.7	1.7	2.0	2.1	-14.4	-16.8	-21.5	-23.8
4.8	1.3	1.3	1.5	1.7	-10.6	-12.9	-15.5	-19.1
5.0	1.0	1.0	1.1	1.3	-7.6	-9.7	-11.0	-14.5

Table S4. Contribution of different energy components in the overall interaction energy calculated by using SAPT2+ in the $CH_3Cl\cdots YH_3$ (Y = N, P, As, Sb) as a function of the C⋯Y separation. All energy components and the total SAPT2+ interaction energy are given in $kJ.mol^{-1}$.

Distance C···Y	E_{elst}	E_{disp}	E_{ind}	δE_{HF}	E_{exch}	E_{SAPT2+}	%elst	%disp	%ind	$\%\delta E_{HF}$
	Y = N									
2.8	-88.3	-36.8	-65.5	-19.3	193.9	-16.0	42.1	17.5	31.2	9.2
3.0	-57.9	-24.7	-34.7	-11.2	104.0	-24.7	45.0	19.2	27.0	8.7
3.2	-39.1	-16.7	-18.8	-6.1	54.8	-25.9	48.5	20.6	23.3	7.6
3.4	-27.4	-11.3	-10.4	-3.3	28.5	-23.9	52.3	21.6	19.9	6.2
3.6	-19.9	-7.9	-6.0	-1.7	14.8	-20.7	56.2	22.1	16.9	4.8
3.8	-15.0	-5.5	-3.6	-0.9	7.6	-17.4	60.1	22.1	14.2	3.6
4.0	-11.7	-4.0	-2.2	-0.5	3.9	-14.4	63.9	21.6	11.9	2.6
4.2	-9.3	-2.9	-1.4	-0.2	2.0	-11.8	67.5	20.7	10.0	1.8
4.4	-7.6	-2.1	-0.9	-0.1	1.0	-9.7	70.7	19.6	8.5	1.2
4.6	-6.3	-1.6	-0.6	-0.1	0.5	-8.0	73.5	18.5	7.2	0.8
4.8	-5.3	-1.2	-0.4	0.0	0.3	-6.7	76.0	17.3	6.2	0.5
5.0	-4.5	-0.9	-0.3	0.0	0.1	-5.6	78.2	16.0	5.4	0.4
	Y = P									
2.8	-119.9	-72.7	-213.4	-10.1	502.0	85.9	28.8	17.5	51.3	2.4
3.0	-78.1	-51.9	-115.8	-16.3	299.4	37.3	29.8	19.8	44.2	6.2
3.2	-50.5	-36.6	-62.3	-13.2	173.4	10.9	31.0	22.5	38.3	8.1
3.4	-32.7	-25.8	-33.6	-8.8	98.4	-2.5	32.5	25.5	33.3	8.7
3.6	-21.6	-18.1	-18.2	-5.3	54.8	-8.4	34.2	28.7	28.8	8.4
3.8	-14.7	-12.8	-10.0	-3.0	30.2	-10.3	36.2	31.6	24.7	7.5
4.0	-10.3	-9.1	-5.6	-1.7	16.5	-10.2	38.6	34.2	21.0	6.3
4.2	-7.5	-6.6	-3.2	-0.9	9.0	-9.2	41.2	36.2	17.5	5.0
4.4	-5.6	-4.8	-1.9	-0.5	4.8	-7.9	44.0	37.6	14.5	3.8
4.6	-4.4	-3.6	-1.1	-0.3	2.6	-6.7	47.0	38.3	12.0	2.7
4.8	-3.5	-2.7	-0.7	-0.1	1.4	-5.6	50.1	38.3	9.8	1.8
5.0	-2.8	-2.0	-0.4	-0.1	0.7	-4.6	53.0	37.7	8.2	1.2

	Y = As									
2.8	-130.5	-78.9	-321.3	5.9	631.0	106.2	24.9	15.0	61.2	-1.1
3.0	-84.4	-56.8	-171.0	-11.8	374.5	50.4	26.0	17.5	52.8	3.6
3.2	-53.8	-40.5	-90.2	-12.9	216.4	19.1	27.3	20.5	45.7	6.5
3.4	-34.2	-28.7	-47.6	-9.6	122.6	2.5	28.5	23.9	39.6	8.0
3.6	-22.0	-20.3	-25.2	-6.3	68.2	-5.5	29.9	27.5	34.1	8.5
3.8	-14.6	-14.4	-13.5	-3.8	37.6	-8.6	31.5	31.2	29.1	8.2
4.0	-10.0	-10.3	-7.4	-2.2	20.6	-9.3	33.6	34.5	24.6	7.3
4.2	-7.2	-7.5	-4.1	-1.2	11.2	-8.7	35.9	37.4	20.6	6.1
4.4	-5.3	-5.5	-2.3	-0.6	6.1	-7.7	38.6	39.7	17.0	4.7
4.6	-4.1	-4.0	-1.4	-0.3	3.3	-6.5	41.6	41.2	14.0	3.2
4.8	-3.2	-3.0	-0.8	-0.1	1.8	-5.5	44.8	42.0	11.4	1.8
5.0	-2.6	-2.3	-0.5	0.0	1.0	-4.5	47.8	42.1	9.4	0.8
	Y = Sb									
2.8	-132.0	-95.0	-303.5	20.1	690.1	179.7	25.9	18.6	59.5	-3.9
3.0	-89.1	-70.4	-178.8	-7.8	444.8	98.7	25.7	20.3	51.7	2.2
3.2	-58.6	-51.3	-103.2	-13.8	276.5	49.6	25.8	22.6	45.5	6.1
3.4	-37.8	-37.0	-58.7	-11.9	166.7	21.3	26.0	25.5	40.4	8.2
3.6	-24.2	-26.7	-33.3	-8.3	98.4	5.9	26.1	28.8	36.0	9.0
3.8	-15.5	-19.2	-18.8	-5.3	56.9	-1.9	26.4	32.7	32.0	8.9
4.0	-10.1	-13.9	-10.7	-3.2	32.5	-5.3	26.7	36.6	28.3	8.3
4.2	-6.7	-10.1	-6.2	-1.8	18.4	-6.4	27.1	40.6	24.8	7.4
4.4	-4.6	-7.4	-3.6	-1.0	10.3	-6.3	27.7	44.4	21.5	6.3
4.6	-3.2	-5.5	-2.1	-0.6	5.8	-5.6	28.4	48.0	18.4	5.2
4.8	-2.3	-4.1	-1.3	-0.3	3.2	-4.8	29.2	51.0	15.7	4.1
5.0	-1.7	-3.1	-0.8	-0.2	1.8	-4.0	30.1	53.4	13.3	3.2