Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Cooperative Halogen Bonds in V-Shaped $H_3N{\cdot}X1X2{\cdot}X3Y$(X1, X2, X3=Cl and Br; Y=F, Cl and Br) Complexes

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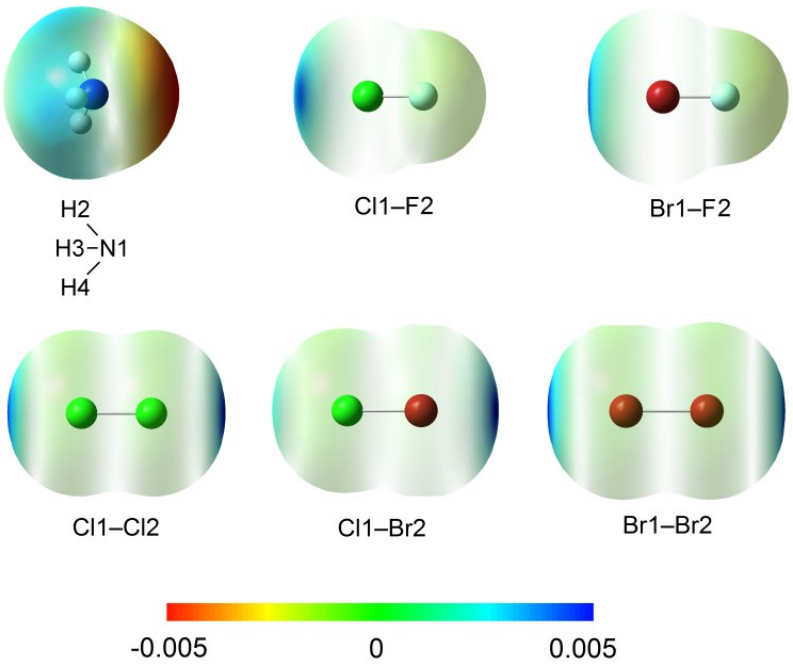

Figure S1. Optimized geometries for the six monomers (NH_3, FCl, FBr, Cl_2, ClBr, Br_2) and their MEPs mapped on the surface of molecular electron density (0.0004 a.u.). The values of the MEP are in the range from –0.005 to 0.005 a.u.

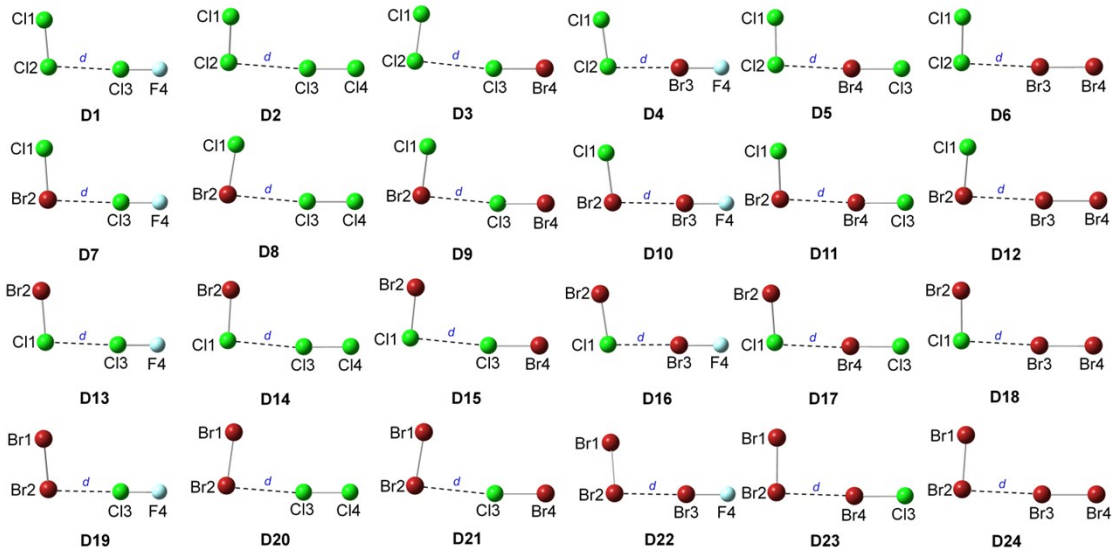

Figure S2. Optimized structures of dimers **D1-24**.

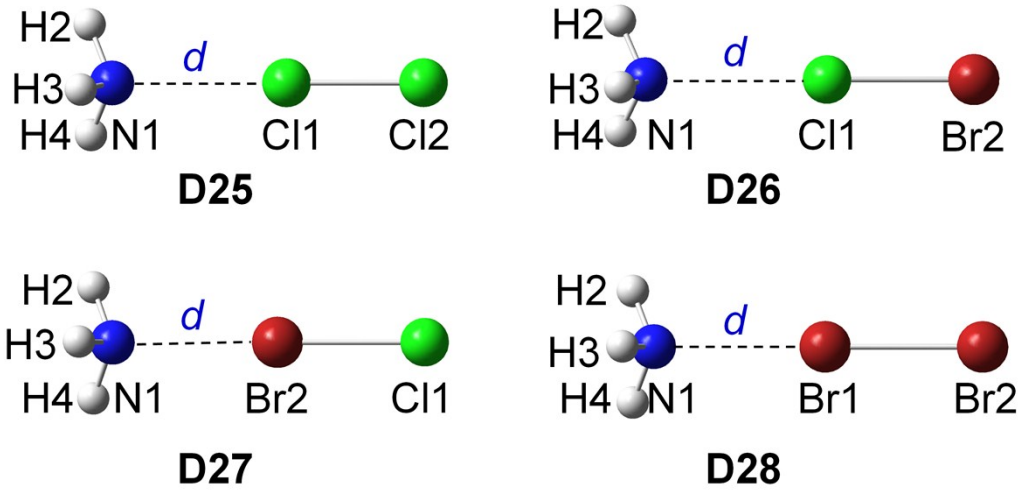

Figure S3. Optimized structures of dimers **D25-28**.

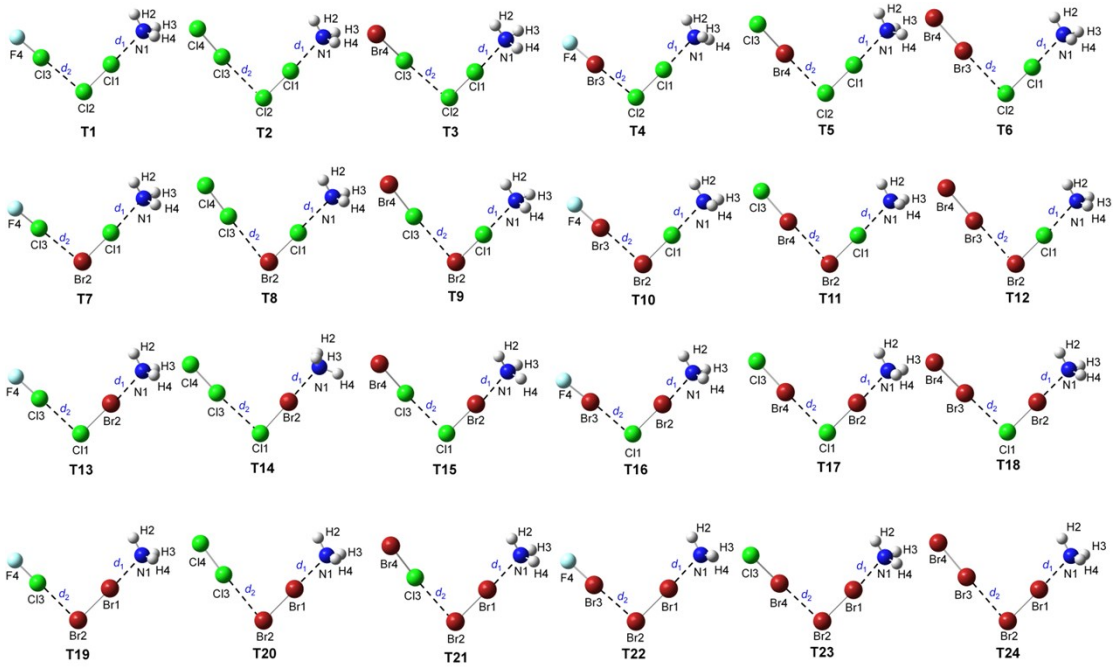

Figure S4. Optimized structures of trimers **T1-24**.

Table S1 Structural parameters (*R*, in Å) and stretching vibrational frequencies (ν, in cm^{-1}) of six monomers at the MP2/aug-cc-pVTZ level.

Monomer	Bond	*R*	*v*
NH_3	N1-H2	1.0121	3503.1
ClF	Cl1-F2	1.6383	799.9
BrF	Br1-F2	1.7584	691.8
Cl_2	Cl1-Cl2	1.9987	573.5
ClBr	Cl1-Br2	2.1383	460.6
Br_2	Br1-Br2	2.2787	341.2

Table S2 Structural parameters (R, d, in Å), stretching vibrational frequencies (v, in cm^{-1}) and interaction energies (ΔE_{int}, in kcal mol^{-1}) of dimers **D1-24** obtained at the MP2/aug-cc-pVTZ level without (non-CP) CP optimization.

Complex	Bond	R	v	d	ΔE_{int}
D1	Cl1-Cl2	1.9984	572.5	2.9940	-2.64
	Cl3-F4	1.6459	776.6		
D2	Cl1-Cl2	1.9986	572.8	3.2264	-2.03
	Cl3-Cl4	2.0025	565.9		
D3	Cl1-Cl2	1.9985	573.0	3.2680	-2.05
	Cl3-Br4	2.1411	456.1		
D4	Cl1-Cl2	1.9980	572.1	2.9535	-4.02
	Br3-F4	1.7690	668.0		
D5	Cl1-Cl2	1.9986	572.4	3.1777	-3.00
	Cl3-Br4	2.1454	451.5		
D6	Cl1-Cl2	1.9986	572.6	3.2341	-2.91
	Br3-Br4	2.2843	336.0		
D7	Cl1-Br2	2.1357	461.5	3.0125	-3.35
	Cl3-F4	1.6504	760.4		
D8	Cl1-Br2	2.1371	461.0	3.2703	-2.48
	Cl3-Cl4	2.0046	560.8		
D9	Cl1-Br2	2.1373	461.0	3.3130	-2.50
	Cl3-Br4	2.1428	453.0		
D10	Cl1-Br2	2.1360	459.9	2.9774	-5.07
	Br3-F4	1.7753	652.8		
D11	Cl1-Br2	2.1367	460.9	3.2146	-3.66
	Cl3-Br4	2.1494	445.3		
D12	Cl1-Br2	2.1371	460.6	3.2742	-3.53
	Br3-Br4	2.2873	332.1		
D13	Cl1-Br2	2.1389	459.6	2.9678	-3.10
	Cl3-F4	1.6470	773.5		
D14	Cl1-Br2	2.1388	459.7	3.2010	-2.42
	Cl3-Cl4	2.0032	564.6		
D15	Cl1-Br2	2.1385	459.9	3.2453	-2.42
	Cl3-Br4	2.1416	455.8		
D16	Cl1-Br2	2.1395	458.6	2.9317	-4.63
	Br3-F4	1.7706	665.0		
D17	Cl1-Br2	2.1391	459.3	3.1517	-3.51
	Cl3-Br4	2.1465	450.0		
D18	Cl1-Br2	2.1390	459.3	3.2080	-3.41
	Br3-Br4	2.2852	335.1		
D19	Br1-Br2	2.2774	341.3	2.9953	-3.78
	Cl3-F4	1.6518	756.3		

D20	Br1-Br2	2.2782	341.1	3.2523	-2.84
	Cl3-Cl4	2.0054	559.2		
D21	Br1-Br2	2.2781	341.1	3.2966	-2.85
	Cl3-Br4	2.1434	452.0		
D22	Br1-Br2	2.2778	340.4	2.9661	-5.63
	Br3-F4	1.7769	649.8		
D23	Br1-Br2	2.2779	341.0	3.1975	-4.15
	Cl3-Br4	2.1504	444.0		
D24	Br1-Br2	2.2781	340.9	3.2545	-4.01
	Br3-Br4	2.2885	330.9		

Table S3 Structural parameters (R, d, in Å), stretching vibrational frequencies (v, in cm^{-1}) and interaction energies (ΔE_{int}, $\Delta E_{int,CP}$, in kcal mol^{-1}) of dimers **D25-28** without (Non-CP) and with CP optimizations at the MP2/aug-cc-pVTZ level.

Complex	Bond	non-CP				CP			
		R	v	d	ΔE_{int}	R	v	d	$\Delta E_{int,CP}$ (δ_{BSSE})
D25	N1-H2	1.0123	3498.4	2.5907	-5.48	1.0124	3498.5	2.6333	-4.93 (0.55)
	Cl1-Cl2	2.0335	505.8			2.0295	513.2		
D26	N1-H2	1.0124	3498.4	2.6776	-4.53	1.0124	3498.2	2.7332	-3.86 (0.67)
	Cl1-Br2	2.1640	416.0			2.1609	421.5		
D27	N1-H2	1.0126	3493.3	2.4698	-10.08	1.0125	3496.0	2.5288	-8.46 (1.62)
	Cl1-Br2	2.2026	398.9			2.1933	400.5		
D28	N1-H2	1.0125	3494.4	2.5385	-8.60	1.0126	3494.4	2.6103	-6.89 (1.70)
	Br1-Br2	2.3322	294.0			2.3236	299.1		

Table S4 Structural parameters (R, d_1, d_2, in Å), stretching vibrational frequencies (v, in cm^{-1}) and interaction energies (ΔE_{int}, in kcal mol^{-1}) of trimers **T1-24** without CP optimizations at the MP2/ aug-cc-pVTZ level.

Complex	Bond	R	v	d_1	d_2	ΔE_{int}
T1	N1-H2	1.0126	3495.4	2.4627	2.8726	-9.69
	Cl1-Cl2	2.0533	468.6			
	Cl3-F4	1.6548	754.2			
T2	N1-H2	1.0125	3496.4	2.5225	3.1434	-8.31
	Cl1-Cl2	2.0438	486.1			
	Cl3-Cl4	2.0054	560.4			
T3	N1-H2	1.0125	3496.7	2.5354	3.1968	-8.14
	Cl1-Cl2	2.0413	490.5			
	Cl3-Br4	2.1435	452.6			
T4	N1-H2	1.0126	3494.5	2.3900	2.8209	-12.00
	Cl1-Cl2	2.0696	443.8			
	Br3-F4	1.7827	643.4			
T5	N1-H2	1.0125	3495.7	2.4662	3.0599	-9.97
	Cl1-Cl2	2.0532	469.5			
	Cl3-Br4	2.1532	441.9			
T6	N1-H2	1.0125	3496.0	2.4863	3.1260	-9.64
	Cl1-Cl2	2.0493	475.8			
	Br3-Br4	2.2900	330.5			
T7	N1-H2	1.0126	3495.7	2.5541	2.9208	-9.28
	Cl1-Br2	2.1759	390.8			
	Cl3-F4	1.6602	734.2			
T8	N1-H2	1.0126	3496.3	2.6120	3.2052	-7.71
	Cl1-Br2	2.1699	403.6			
	Cl3-Cl4	2.0084	553.3			
T9	N1-H2	1.0125	3496.6	2.6237	3.2574	-7.57
	Cl1-Br2	2.1687	406.0			
	Cl3-Br4	2.1453	448.4			
T10	N1-H2	1.0126	3495.0	2.4905	2.8878	-11.77
	Cl1-Br2	2.1859	373.7			
	Br3-F4	1.7886	628.2			

T11	N1-H2	1.0127	3494.7	2.5595	3.1237	-9.51
	Cl1-Br2	2.1762	391.4			
	Cl3-Br4	2.1577	435.1			
T12	N1-H2	1.0125	3496.3	2.5761	3.1877	-9.17
	Cl1-Br2	2.1742	395.5			
	Br3-Br4	2.2939	325.5			
T13	N1-H2	1.0129	3489.7	2.3716	2.7995	-15.66
	Cl1-Br2	2.2297	373.6			
	Cl3-F4	1.6622	734.8			
T14	N1-H2	1.0127	552.3	2.4147	3.0725	-13.77
	Cl1-Br2	2.2169	381.5			
	Cl3-Cl4	2.0097	3491.8			
T15	N1-H2	1.0127	3492.0	2.4243	3.1295	-13.49
	Cl1-Br2	2.2142	383.3			
	Cl3-Br4	2.1460	448.1			
T16	N1-H2	1.0132	3486.9	2.3294	2.7660	-18.53
	Cl1-Br2	2.2452	365.5			
	Br3-F4	1.7909	628.8			
T17	N1-H2	1.0130	3488.7	2.3735	2.9839	-15.95
	Cl1-Br2	2.2298	372.9			
	Cl3-Br4	2.1602	433.9			
T18	N1-H2	1.0129	3490.4	2.3864	3.0449	-15.47
	Cl1-Br2	2.2256	375.6			
	Br3-Br4	2.2958	324.7			
T19	N1-H2	1.0129	3490.3	2.4309	2.8594	-14.65
	Br1-Br2	2.3549	279.9			
	Cl3-F4	1.6688	711.2			
T20	N1-H2	1.0127	3492.1	2.4778	3.1423	-12.59
	Br1-Br2	2.3442	285.6			
	Cl3-Cl4	2.0124	544.7			
T21	N1-H2	1.0127	3492.7	2.4878	3.1960	-12.34
	Br1-Br2	2.3420	286.9			
	Cl3-Br4	2.1485	442.3			
T22	N1-H2	1.0130	3488.5	2.3897	2.8437	-17.65
	Br1-Br2	2.3664	275.0			

	Br3-F4	1.7977	612.0			
T23	N1-H2	1.0128	3490.6	2.4336	3.0552	-14.90
	Br1-Br2	2.3550	279.6			
	Cl3-Br4	2.1661	424.5			
T24	N1-H2	1.0128	3491.0	2.4468	3.1177	-14.41
	Br1-Br2	2.3517	281.2			
	Br3-Br4	2.3007	318.6			

Table S5 Sum(d) and Δd_D of dimers **D1-28**. [a]

Complex	Sum(d)	Δd_D
D1	3.60	0.5629
D2	3.60	0.3274
D3	3.60	0.2773
D4	3.75	0.7317
D5	3.75	0.4993
D6	3.75	0.4366
D7	3.75	0.6471
D8	3.75	0.3881
D9	3.75	0.3385
D10	3.90	0.8316
D11	3.90	0.5792
D12	3.90	0.5147
D13	3.60	0.5862
D14	3.60	0.3493
D15	3.60	0.2993
D16	3.75	0.7531
D17	3.75	0.5253
D18	3.75	0.4611
D19	3.75	0.6647
D20	3.75	0.4069
D21	3.75	0.3562
D22	3.90	0.8446
D23	3.90	0.6001
D24	3.90	0.5364
D25	3.30	0.6667
D26	3.30	0.5668
D27	3.45	0.9212
D28	3.45	0.8397

[a] Sum(d) is the sum of the van der Waals radii involved in halogen bonding, and Δd_D is the difference between Sum(d) and the halogen bonding distance.

Table S6 Sum(d) and the corresponding Δd_T of the halogen bonding in trimers **T1-24**. [a]

Complex	Sum(d_1)	$\Delta d_{1,T}$	Sum(d_2)	$\Delta d_{2,T}$
T1	3.30	-0.7854	3.60	0.6806
T2	3.30	-0.7287	3.60	0.4094
T3	3.30	-0.7160	3.60	0.3486
T4	3.30	-0.8482	3.75	0.8636
T5	3.30	-0.7757	3.75	0.6152
T6	3.30	-0.7570	3.75	0.5441
T7	3.30	-0.6787	3.75	0.7361
T8	3.30	-0.6239	3.75	0.4499
T9	3.30	-0.6149	3.75	0.3981
T10	3.30	-0.7334	3.90	0.9266
T11	3.30	-0.6685	3.90	0.6701
T12	3.30	-0.6531	3.90	0.5992
T13	3.45	-1.0183	3.60	0.7475
T14	3.45	-0.9759	3.60	0.4750
T15	3.45	-0.9652	3.60	0.4117
T16	3.45	-1.0611	3.75	0.9221
T17	3.45	-1.0110	3.75	0.6908
T18	3.45	-0.9996	3.75	0.6214
T19	3.45	-0.9433	3.75	0.8004
T20	3.45	-0.8964	3.75	0.5102
T21	3.45	-0.8854	3.75	0.4527
T22	3.45	-0.9873	3.90	0.9744
T23	3.45	-0.9378	3.90	0.7384
T24	3.45	-0.9233	3.90	0.6687

[a] Sum(d_1) and Sum(d_2) are the sum of the van der Waals radii involved in halogen bonding corresponding with d_1 and d_2, respectively. Δd_T is the difference between Sum(d) and the binding distance (d_1 or d_2).

Table S7 Topological parameters at the BCPs for dimers **D1-28** (all units are in a.u.).

Complex	Binding	ρ	$\nabla^2\rho$	V	G	H
D1	Cl2···Cl3	0.0135	0.0582	-0.0101	0.0123	0.0022
D2	Cl2···Cl3	0.0086	0.0377	-0.0054	0.0074	0.0020
D3	Cl2···Cl3	0.0080	0.0345	-0.0048	0.0067	0.0019
D4	Cl2···Br3	0.0170	0.0633	-0.0130	0.0144	0.0014
D5	Cl2···Br4	0.0110	0.0427	-0.0072	0.0089	0.0017
D6	Cl2···Br3	0.0099	0.0384	-0.0062	0.0079	0.0017
D7	Br2···Cl3	0.0152	0.0562	-0.0111	0.0126	0.0015
D8	Br2···Cl3	0.0092	0.0361	-0.0056	0.0073	0.0017
D9	Br2···Cl3	0.0085	0.0331	-0.0050	0.0066	0.0016
D10	Br2···Br3	0.0197	0.0612	-0.0146	0.0150	0.0003
D11	Br2···Br4	0.0123	0.0414	-0.0079	0.0091	0.0012
D12	Br2···Br3	0.0110	0.0374	-0.0068	0.0081	0.0013
D13	Cl1···Cl3	0.0143	0.0606	-0.0108	0.0130	0.0022
D14	Cl1···Cl3	0.0091	0.0395	-0.0057	0.0078	0.0021
D15	Cl1···Cl3	0.0084	0.0361	-0.0051	0.0071	0.0020
D16	Cl1···Br3	0.0179	0.0654	-0.0137	0.0150	0.0013
D17	Cl1···Br4	0.0117	0.0447	-0.0077	0.0094	0.0017
D18	Cl1···Br3	0.0105	0.0401	-0.0066	0.0083	0.0017
D19	Br2···Cl3	0.0158	0.0577	-0.0116	0.0130	0.0014
D20	Br2···Cl3	0.0096	0.0374	-0.0059	0.0076	0.0017
D21	Br2···Cl3	0.0089	0.0343	-0.0053	0.0069	0.0016
D22	Br2···Br3	0.0202	0.0620	-0.0150	0.0153	0.0002
D23	Br2···Br4	0.0128	0.0428	-0.0083	0.0095	0.0012
D24	Br2···Br3	0.0115	0.0387	-0.0071	0.0084	0.0013
D25	N1···Cl1	0.0258	0.0960	-0.0209	0.0225	0.0015
D26	N1···Cl1	0.0212	0.0812	-0.0160	0.0181	0.0022
D27	N1···Br2	0.0376	0.1099	-0.0324	0.0299	-0.0024
D28	N1···Br1	0.0320	0.0994	-0.0260	0.0254	-0.0006