Intramolecular pnicogen interactions in phosphorus and arsenic analogues of proton sponges. *Supporting Information*

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- Figure S2. NCI plot of the non-covalent interaction of 1,8-PHF FP···PF (*R,R*) and 1,8-AsHF Fas···AsF (*R,R*), left and right respectively. Blue areas are those with $\lambda_2>0$ (strong attractive), while green ones correspond to $\lambda_2 \approx 0$ (weak). λ_2 is one of the three eigenvalues of the electron density Hessian with $\lambda_1 \leq \lambda_2 \leq \lambda_3$.

- Figure S3. P···P distance vs. P-C-C bond in the X-ray structures found in the CSD search.

Table S1. Comparison between aug'-cc-pVDZ and aug'-cc-pVTZ basis sets. Structural parameters, distance in Å, Dihedral angle in º, at MP2 computational level.

	Distance		Dihedral	
	MP2/avdz	MP2/avtz	MP2/avdz	MP2/avtz
1,8-PH_2	3.038	2.986	17.8	15.6
1,8-PHF FPPF	2.680	2.604	27.5	27.3
1,8-PHF FPPH	2.805	2.731	14.7	15.5
1,8-PF_2	2.970	2.914	27.7	26.7

Table S2. Relative energies respect to the 1,8 derivative (E_{rel}) and interaction energies (E_{iso}) in $kJ \cdot mol^{-1}$, at different computation method, CCSDT(T) and MP2, and two different basis set.

	E_{rel}			
	CCSD(T)/avdz//MP2/avdz	MP2/avdz[a]	MP2/avtz[a]	MP2/avtz//MP2/avdz
1,8-PH_2	0.0	0.0	0.0	0.0
1,5-PH_2 C2	-22.9	-22.0	-20.3	-20.6
1,5-PH_2 Ci	-22.9	-22.0	-20.3	-20.6
1,8-PHF FPPF	0.0	0.0	0.0	0.0
1,8-PHF FPPH	8.5	10.8	11.1	11.0
1,5-PHF C2	4.0	8.6	13.6	12.7
1,5-PHF Ci	3.6	8.3	13.5	12.7
1,8-PF_2	0.0	0.0	0.0	0.0
1,5-PF_2	-10.8	-11.1	-9.35	-11.1
	E_{iso}			
	CCSD(T)/avdz//MP2/avdz	MP2-avdz[a]	MP2-avtz[a]	MP2-avtz//MP2-avdz
1,8-PH_2	23.1	22.2	21.3	21.2
1,5-PH_2 C2	0.2	0.2	0.6	0.6
1,5-PH_2 Ci	0.2	0.1	0.6	0.6
1,8-PHF FPPF	-4.4	-11.3	-13.5	-11.1
1,8-PHF FPPH	4.0	1.5	-1.3	-0.1
1,5-PHF C2	-0.4	1.4	2.0	1.6
1,5-PHF Ci	-0.8	1.1	1.9	1.6
1,8-PF_2	14.0	14.0	13.0	14.0
1,5-PF_2	3.2	2.9	3.7	2.9

[a] from optimized geometries at this level.

Table S3. Z-C-C angles (Ang) and Z-C-C-Z dihedral angles (both in º) of the systems studied at MP2/avtz//MP2/avdz computational level.

System and alignment		Sym	Ang[a]	Dihedral Ang[b]			Sym	Ang[a]	Dihedral Ang[b]
1,8-PHF					1,8-AsHF				
FPPF	*R, R*	C_2	118.7	27.5	FAsAsF	*R, R*	C_2	120.7	27.3
FPPH	*R, S*	C_1	123.9 (118.7)[c]	14.7	FAsAsH	*R, S*	C_1	125.6 (120.3)[c]	12.0
HPPH	*R, R*	C_2	123.5	10.9	HAsAsH	*R, R*	C_2	124.5	10.0
1,5-PHF	*R, R*	C_2			1,5-AsHF	*R, R*	C_2		
	R, S	C_i				*R, S*	C_i		
1,8-PHCl					1,8-AsHCl				
ClPPCl	*R, R*	C_2	117.2	30.3	ClAsAsCl	*R, R*	C_2	118.8	31.2
ClPPH	*R, S*	C_1	120.51 (120.0)[c]	22.5	ClAsAsH	*R, S*	C_1	122.0 (121.0)[c]	22.2
HPPH	*R, R*	C_2	123.8	1.9	HAsAsH	*R, R*	C_2	124.7	5.0
1,5-PHCl	*R, R*	C_2			1,5-AsHCl	*R, R*	C_2		
	R, S	C_i				*R, S*	C_i		
1,8-PHBr					1,8-AsHBr				
BrPPBr	*R, R*	C_2	116.5	30.8	BrAsAsBr	*R, R*	C_2	118.3	32.1
BrPPH	*R, S*	C_1	119.8 (120.0)[c]	24.7	BrAsAsH	*R, S*	C_1	121.2 (121.0)[c]	24.9
HPPH	*R, R*	C_2	123.6	6.3	HAsAsH	*R, R*	C_2	124.5	9.2
1,5-PHBr	*R, R*	C_2			1,5-AsHBr	*R, R*	C_2		
	R, S	C_i				*R, S*	C_i		
1,8-PH_2	-	C_2	123.5	17.8	1,8-AsH2	-	C_2	124.0	20.6

1,5-PH_2	-	C_2			1,5-AsH2	-	C_2		
	-	C_i				-	C_i		
1,8-PF_2	-	C_1	121.4	27.7	1,8-AsF_2	-	C_1	122.9	27.1
1,5-PF_2	-	C_2			1,5-AsF_2	-	C_2		
	-	C_i				-	C_2		
1,8-PCl_2	-	C_2	118.3	32.6	1,8-$AsCl_2$	-	C_2	119.7	33.6
1,5-PCl_2	-	C_2			1,5-$AsCl_2$	-	C_2		
	-	C_i				-	C_i		
1,8-PBr_2	-	C_2	117.2	33.1	1,8-$AsBr_2$	-	C_2	118.8	34.3
1,5-PBr_2	-	C_2			1,5-$AsBr_2$	-	C_2		
	-	C_i				-	C_i		

[a] Angle correspond to that formed by Z-C1-C2 atoms, in which C2 is the atom shared by the two rings.

[b] Dihedral angle correspond to that formed by C-Z···Z-C atoms.

[c] Number in parenthesis correspond to the angle in the group with Z-H alignment.

Table S4. Electron density (ρ), Laplacian ($\nabla^2\rho$), electron potential density (V), kinetic energy density (G), C ratio and total electron density energy (H) at MP2/aug'-cc-pVDZ computational level.

	Steoch.	ρ	$\nabla^2\rho$	V	G	C	H
1,8-PH_2		0.0194	0.0409	-0.0103	0.0103	1.0041	0.0000
1,8-PHF							
FPPF	R,R	0.0425	0.0340	-0.0264	0.0174	1.5121	-0.0089
FPPH	R,S	0.0326	0.0440	-0.0190	0.0150	1.2659	-0.0040
HPPH	R,R	0.0232	0.0429	-0.0120	0.0114	1.0555	-0.0006
1,8-PHCl							
ClPPCl	R,R	0.0442	0.0332	-0.0273	0.0178	1.5342	-0.0095
ClPPH	R,S	0.0307	0.0444	-0.0175	0.0143	1.2231	-0.0032
HPPH	R,R	0.0236	0.0448	-0.0128	0.0120	1.0658	-0.0008
1,8-PHBr							
BrPPBr	R,R	0.0487	0.0276	-0.0308	0.0188	1.6340	-0.0119
BrPPH	R,S	0.0311	0.0447	-0.0178	0.0145	1.2272	-0.0033
HPPH	R,R	0.0237	0.0456	-0.0130	0.0122	1.0673	-0.0008

1,8-PF_2		0.0233	0.0424	-0.0124	0.0115	1.0765	-0.0009
1,8-PCl_2		0.0319	0.0450	-0.0183	0.0148	1.2400	-0.0036
1,8-PBr_2		0.0383	0.0429	-0.0230	0.0169	1.3636	-0.0061
	Steoch.	ρ	$\nabla^2\rho$	V	G	C	H
1,8-AsH_2		0.0190	0.0384	-0.0101	0.0099	1.027	-0.0003
1,8-AsHF							
FAsAsF	R,R	0.0324	0.0367	-0.0191	0.0141	1.350	-0.0049
FAsAsH	R,S	0.0277	0.0418	-0.0159	0.0132	1.208	-0.0027
HAsAsH	R,R	0.0214	0.0390	-0.0111	0.0104	1.063	-0.0007
1,8-AsHCl							
ClAsAsCl	R,R	0.0355	0.0357	-0.0210	0.0149	1.403	-0.0060
ClAsAsH	R,S	0.0276	0.0405	-0.0156	0.0129	1.212	-0.0027
HAsAsH	R,R	0.0222	0.0409	-0.0120	0.0111	1.082	-0.0009
1,8-AsHBr							
BrAsAsBr	R,R	0.0375	0.0346	-0.0223	0.0155	1.441	-0.0068
BrAsAsH	R,S	0.0278	0.0406	-0.0157	0.0129	1.213	-0.0028
HAsAsH	R,R	0.0223	0.0416	-0.0123	0.0114	1.085	-0.0010
1,8-AsF2		0.0198	0.0362	-0.0103	0.0097	1.066	-0.0006
1,8-AsCl2		0.0270	0.0393	-0.0150	0.0124	1.210	-0.0026
1,8-AsBr2		0.0311	0.0394	-0.0179	0.0139	1.289	-0.0040

Table S5. AIM charges

	Charge on unit 1				Charge on unit 2			
	P1-X	X	H	P1XH	P2-H	X	H	P2XH
1,8-PHF								
FPPF	1.962	-0.815	-0.593	0.554				
FPPH	1.930	-0.817	-0.598	0.514	1.997	-0.812	-0.584	0.601
HPPH	1.974	-0.815	-0.596	0.563				
1,5-PHF	1.974	-0.811	-0.596	0.567				
	1.976	-0.811	-0.596	0.568				
1-PHF	1.974	-0.812	-0.598	0.565				
1,8-PHCl								

ClPPCl	1.675	-0.559	-0.582	0.534				
ClPPH	1.667	-0.566	-0.586	0.515	1.713	-0.569	-0.578	0.566
HPPH	1.700	-0.567	-0.584	0.549				
1,5-PHCl	1.708	-0.561	-0.587	0.560				
	1.707	-0.562	-0.587	0.559				
1-PHCl	1.704	-0.563	-0.588	0.553				
1,8-PHBr								
BrPPBr	1.511	-0.400	-0.580	0.531				
BrPPH	1.503	-0.403	-0.583	0.516	1.526	-0.388	-0.577	0.561
HPPH	1.527	-0.395	-0.582	0.550				
1,5-PHBr	1.536	-0.390	-0.585	0.561				
	1.538	-0.392	-0.585	0.561				
1-PHBr	1.535	-0.395	-0.587	0.554				
		align	perp					
	P1-X1	X1	X2	$P1X_2$				
1,8-PH_2	1.725	-0.586	-0.579	0.559				
1,5-PH_2	1.736	-0.582	-0.577	0.000				
	1.735	-0.581	-0.577	0.577				
1-PH_2	1.736	-0.581	-0.578	0.577				
1,8-PF_2	2.176	-0.810	-0.811	0.555				
1,5-PF_2	2.186	-0.808	-0.811	0.567				
	2.184	-0.809	-0.811	0.565				
1-PF_2	2.183	-0.809	-0.812	0.562				
1,8-PCl_2	1.613	-0.538	-0.546	0.529				
1,5-PCl_2	1.632	-0.553	-0.538	0.542				
	1.632	-0.552	-0.538	0.541				
1-PCl_2	1.630	-0.554	-0.541	0.535				
1,8-PBr_2	1.222	-0.351	-0.346	0.526				
1,5-PBr_2	1.243	-0.352	-0.349	0.542				
	1.244	-0.352	-0.351	0.542				
1-PBr_2	1.246	-0.357	-0.355	0.534				
	As1-X	X	H	As1XH	As2-H	X	H	As2XH
1,8-AsHF								
FAsAsF	1.358	-0.726	-0.316	0.315				
FAsAsH	1.360	-0.733	-0.327	0.300	1.380	-0.718	-0.313	0.348

HAsAsH	1.397	-0.727	-0.333	0.336				
1,5-AsHF	1.393	-0.722	-0.334	0.337				
	1.392	-0.723	-0.334	0.335				
1-AsHF	1.390	-0.723	-0.337	0.330				
1,8-AsHCl								
ClAsAsCl	1.123	-0.521	-0.300	0.302				
ClAsAsH	1.140	-0.527	-0.310	0.303	1.135	-0.510	-0.302	0.322
HAsAsH	1.158	-0.523	-0.315	0.319				
1,5-AsHCl	1.155	-0.516	-0.317	0.322				
	1.157	-0.518	-0.317	0.322				
1-AsHCl	1.154	-0.520	-0.319	0.315				
1,8-AsHBr								
BrAsAsBr	1.019	-0.422	-0.297	0.301				
BrAsAsH	1.039	-0.426	-0.307	0.306	1.024	-0.404	-0.301	0.319
HAsAsH	1.156	-0.523	-0.315	0.317				
1,5-AsHBr	1.052	-0.413	-0.314	0.325				
	1.053	-0.415	-0.314	0.323				
1-AsHBr	1.049	-0.418	-0.316	0.315				
	As1-X1	X1	X2	$As1X_2$				
1,8-AsH_2	1.002	-0.334	-0.320	0.348				
1,5-AsH_2	1.008	-0.326	-0.322	0.360				
	1.008	-0.326	-0.322	0.359				
1-AsH_2	1.002	-0.326	-0.326	0.350				
1,8-AsF_2	1.733	-0.712	-0.712	0.309				
1,5-AsF_2	1.748	-0.714	-0.713	0.322				
	1.750	-0.714	-0.713	0.322				
1-AsF_2	1.743	-0.716	-0.715	0.313				
1,8-$AsCl_2$	1.259	-0.488	-0.486	0.285				
1,5-$AsCl_2$	1.278	-0.491	-0.487	0.300				
	1.278	-0.492	-0.487	0.299				
1-$AsCl_2$	1.275	-0.496	-0.492	0.287				
1,8-$AsBr_2$	1.034	-0.377	-0.373	0.284				
1,5-$AsBr_2$	1.056	-0.373	-0.380	0.302				
	1.057	-0.373	-0.383	0.301				
1-$AsBr_2$	1.053	-0.379	-0.387	0.288				

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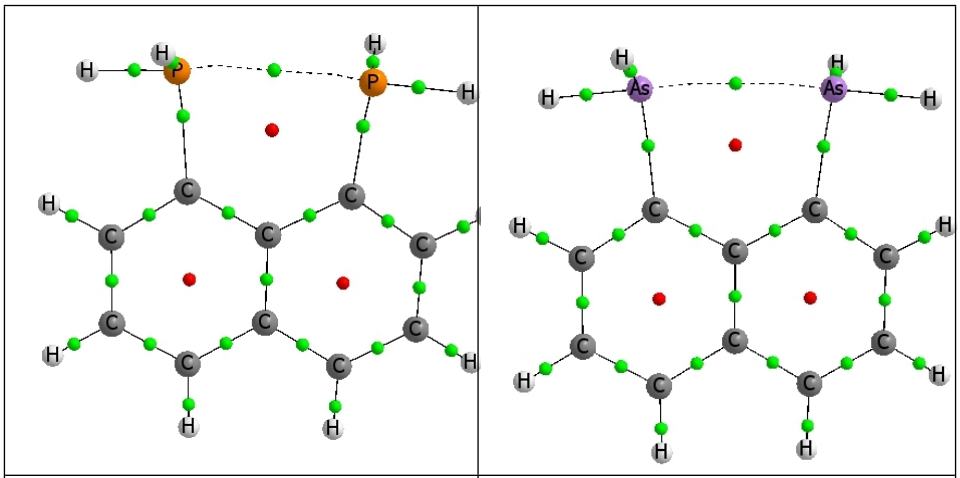
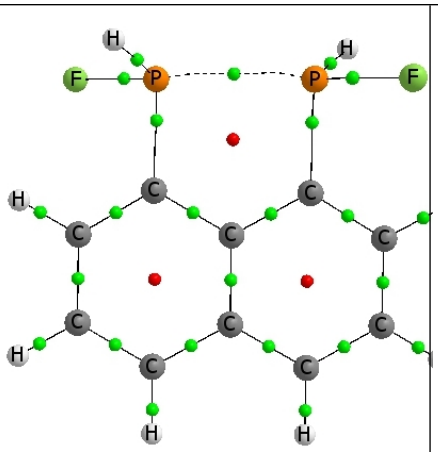
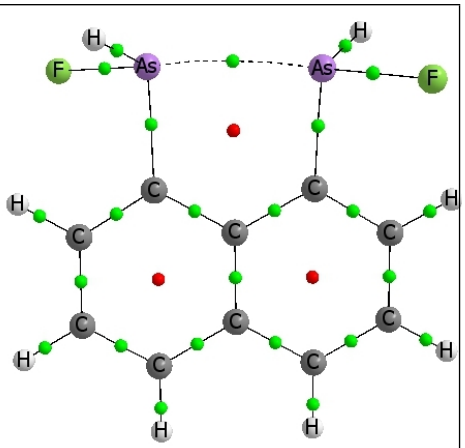
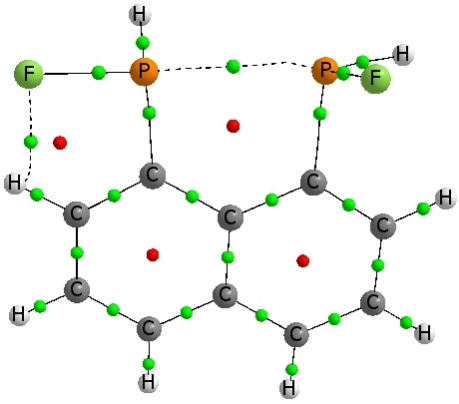
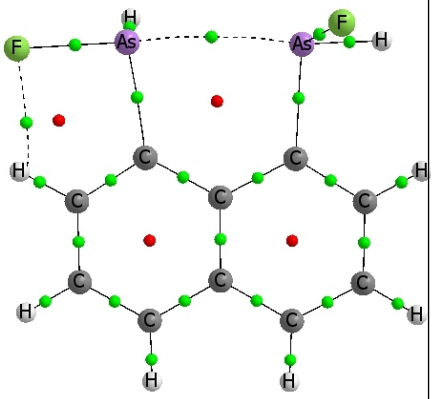
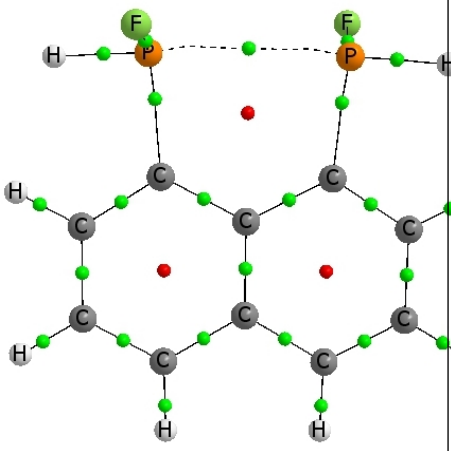
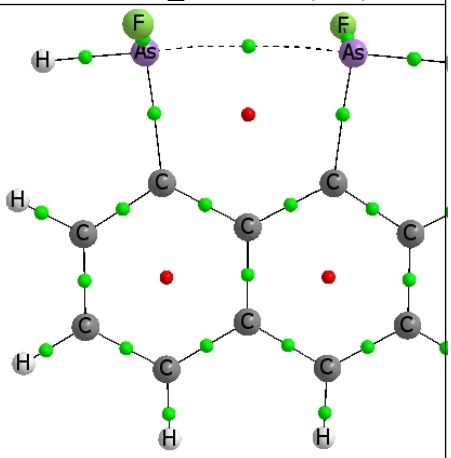
Table S6. 1,8-bis-phosphine derivatives found in the CSD database with some of their geometrical characteristics

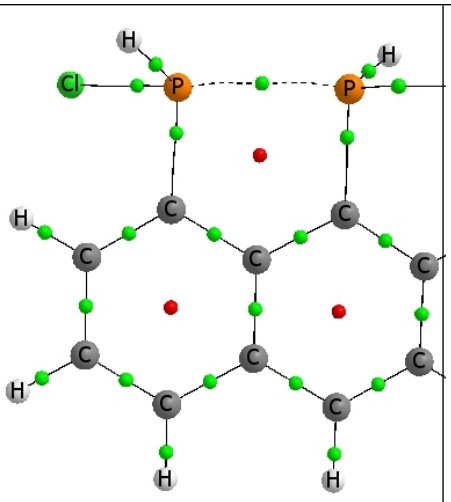
Refcode	P···P dist (Å)	av. P-C-C(º)	C-P···P-C (º)
GUTJIO	2.767	116.8	33.9
GUTJEK	2.798	118.5	23.5
GUTJEK	2.811	119.4	20.5
MIRJIG	2.909	121.9	10.4
ULIJAA	2.912	121.8	11.4
JUHJOL	2.927	122.2	12.0
JUHKOM	2.935	122.3	4.5
JUHJOL	2.944	122.2	10.9
FAKQAK	2.985	123.8	1.3
RESNUY	3.036	123.1	16.9
LAYTOU01	3.048	123.1	14.8
LAYTOU	3.052	123.7	14.9
JUHKUS	3.056	118.2	39.1
RESNUY	3.070	121.6	25.8
RIXYIG	3.117	122.9	20.6
MOGDUH	3.119	123.2	21.3
RIXYIG	3.124	123.2	22.5
NIKGOE	3.125	118.8	37.6
NIKGOE	3.188	119.8	37.0
NIKGOE	3.235	119.3	38.6
NIKGOE	3.272	118.9	42.0

Figure S1.AIM molecular graph for all the compounds considered. Green and red dots indicate bond critical (BCP) and ring critical (RCP) points.

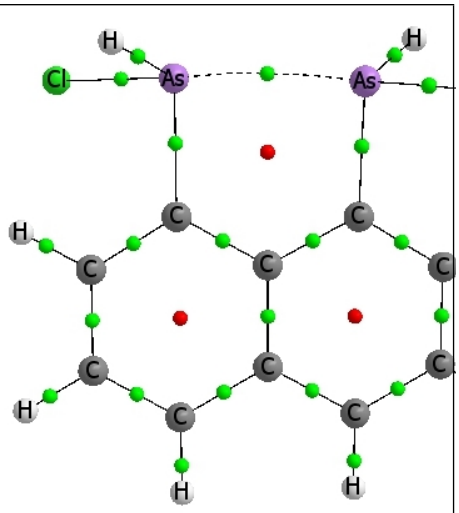


1,8-PH_2 | 1,8-AsH_2

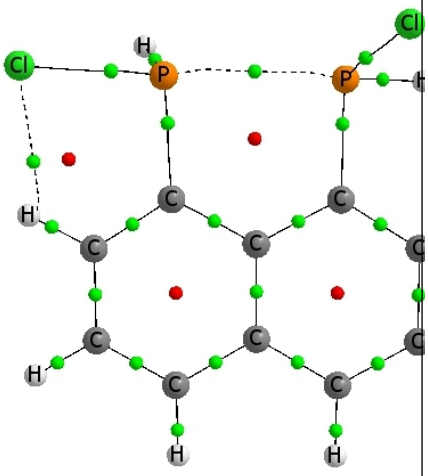
	
1,8-PHF_FPPF (R,R)	1,8-AsHF_FAsAsF (R,R)
	
1,8-PHF_FPPH (R,S)	1,8-AsHF_FAsAsH (R,S)
	
1,8-PHF_HPPH (R,R)	1,8-AsHF_HAsAsH (R,R)



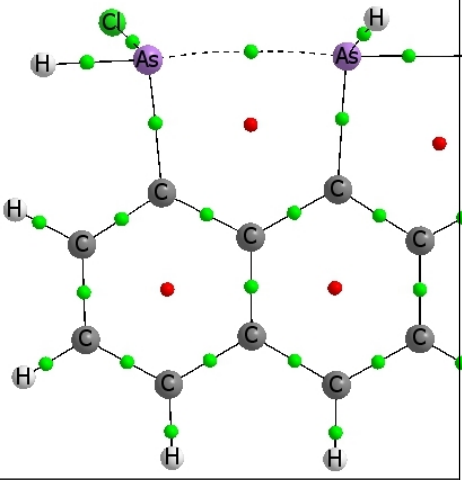
1,8-PHCl_ClPPCl (R,R)



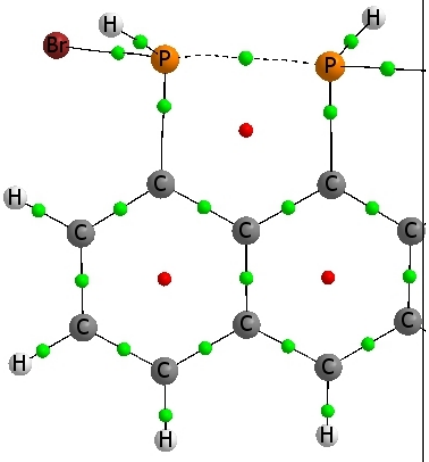
1,8-AsHCl_ClAsAsCl (R,R)



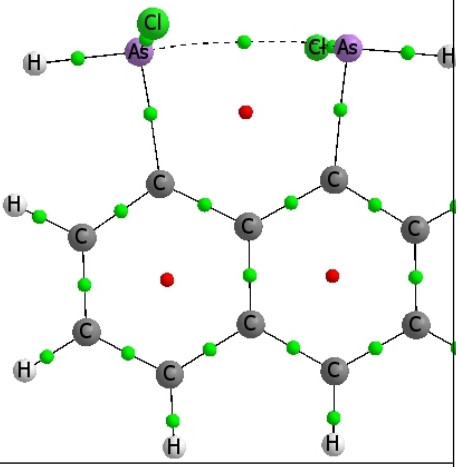
1,8-PHCl_ClPPH (R,S)



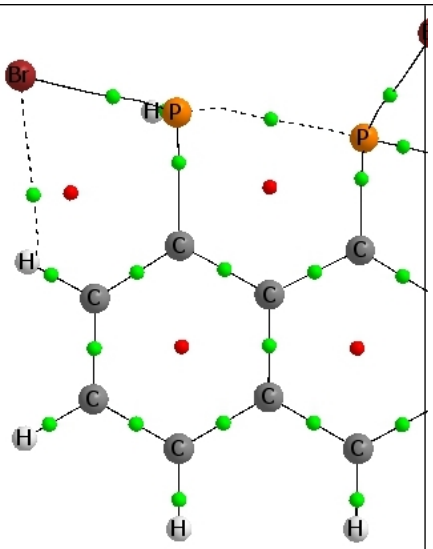
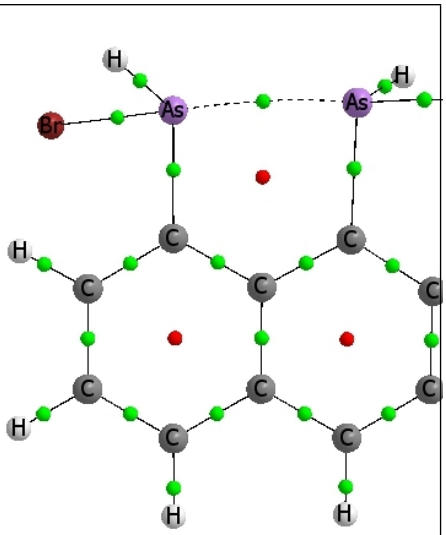
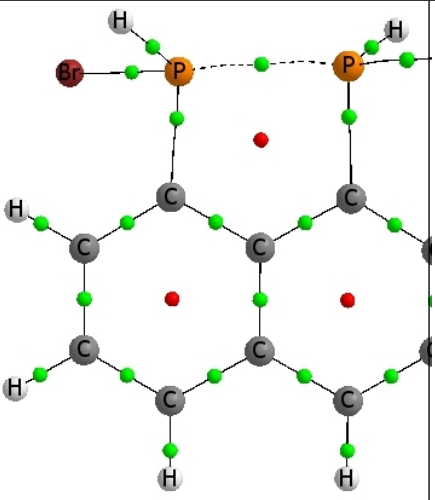
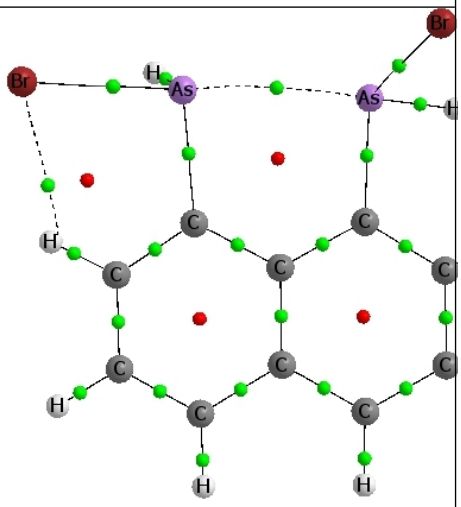
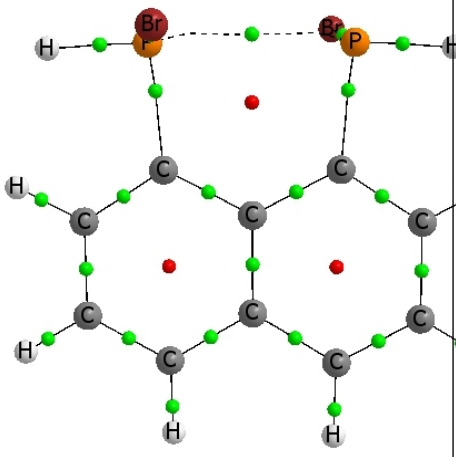
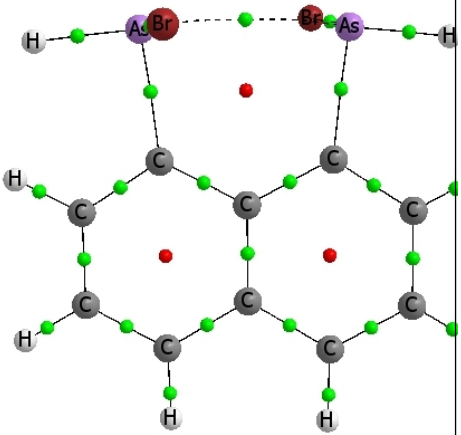
1,8-AsHCl_ClAsAsH (R,S)



1,8-PHCl_HPPH (R,S)



1,8-AsHCl_HAsAsH (R,S)

	
1,8-PHBr_BrPPBr (R,R)	1,8-AsHBr_BrAsAsBr (R,R)
	
1,8-PHBr_BrPPH (R,S)	1,8-AsHBr_BrAsAsH (R,S)
	
1,8-PHBr_HPPH (R,R)	1,8-AsHBr_HAsAsH (R,R)

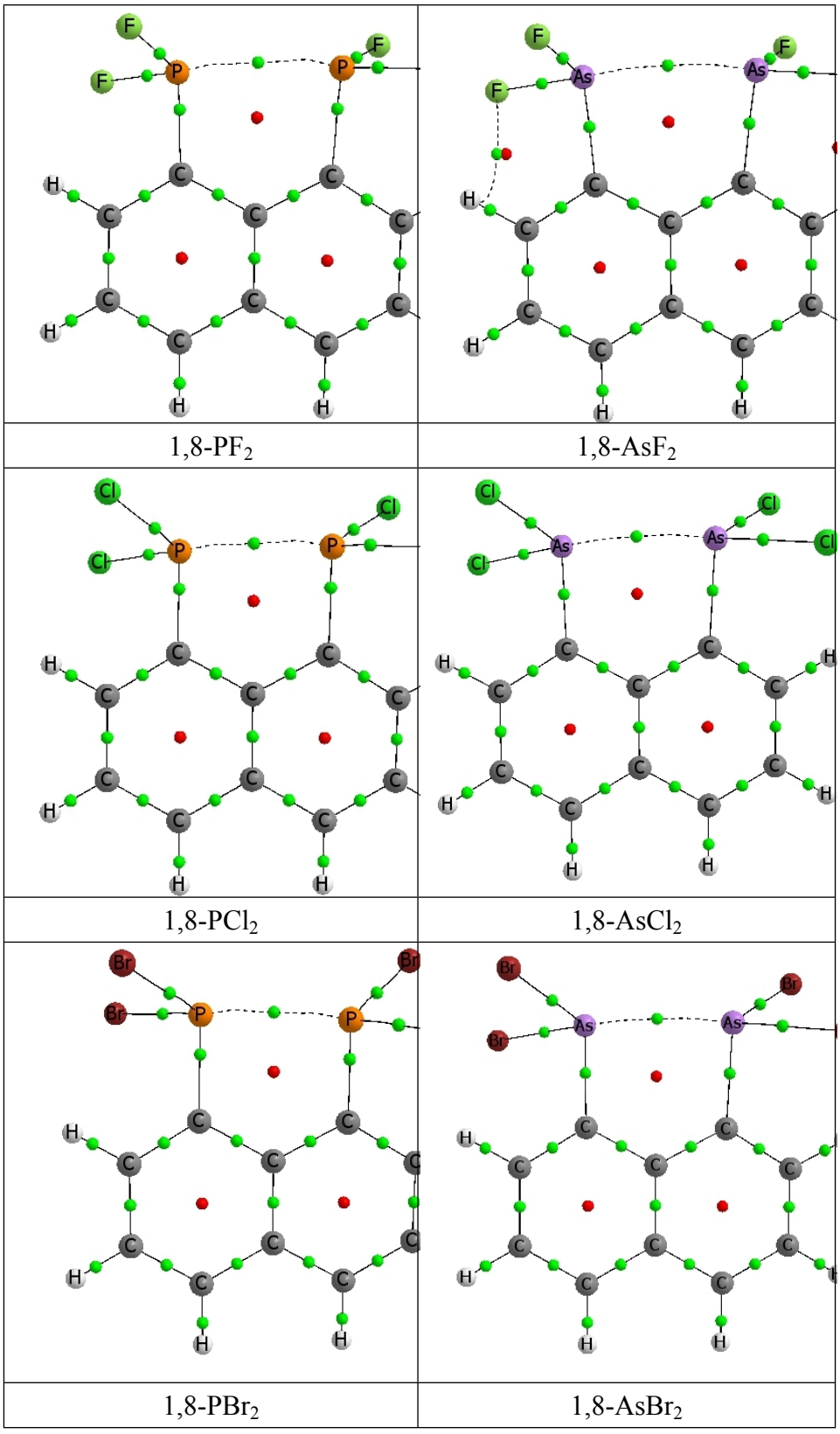
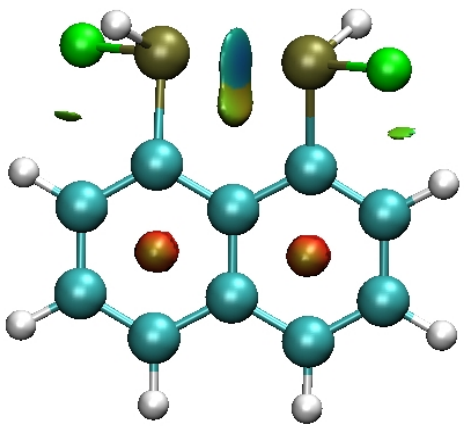
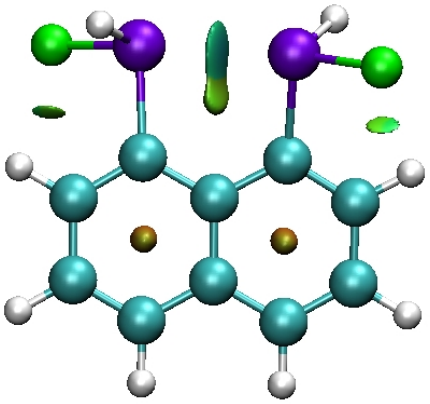


Figure S2. NCI plot of the non-covalent interaction of 1,8-PHF FPPF (*R,R*) and 1,8-AsHF FAsAsF (*R,R*), left and right respectively. Blue areas are those with $\lambda_2>0$ (strong

attractive), while green ones correspond to $\lambda_2 \approx 0$ (weak). λ_2 is one of the three eigenvalues of the electron density Hessian with $\lambda_1 \leq \lambda_2 \leq \lambda_3$.



1,8-PHF FPPF (*R,R*)



1,8-AsHF FAsAsF (*R,R*)

Figure S3. P···P distance vs. P-C-C bond in the X-ray structures found in the CSD search.