Intramolecular pnicogen interactions in phosphorus and arsenic analogues of proton sponges

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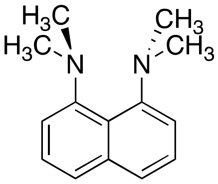
ABSTRACT

A computational study of the intramolecular pnicogen bond in 1,5- and 1,8-bis-substituted naphthalene derivatives (ZXH and ZX_2 with Z = P, As and X = H, F, Cl, and Br), structurally related to proton sponges, has been carried out. The aim of this paper is the study of their structural parameters, interaction energies and electronic properties such as electron density on the intramolecular interaction. The calculated geometrical parameters associated to the P···P interaction are in reasonable good agreement with the crystal structures found in the CSD search, in special those of the halogen derivatives. Isodesmic reactions where the 1,8-bis-subtituted derivatives are compared to monosubstituted derivatives have been calculated, indicating that the 1,8 derivatives are more stable than the monosusbtituted ones for those cases with X-Z···Z-X and F-Z···Z-H alignments. Electron densities and Laplacians at the BCP on the pnicogen interactions suggest that they can be classified as pure closed shell interactions with a partial covalent character. Electron density shift maps are consistent with the results for intermolecular pnicogen interactions. Relationships between interatomic distance and electron density at the bond critical points and between interatomic distance and the orbital charge transfer stabilization energies have been found.

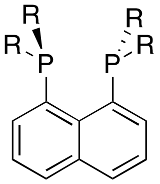
1. INTRODUCTION

Although today "proton sponges" cover a large field moving towards "superbases",[1-5] it all originated from Alder's work.[6] In 1968, this author reported the remarkable basicity of 1,8-bis(dimethylamino)naphthalene (DMAN), trademarked by Aldrich as Proton Sponge. Since then, many investigations into derivatives of DMAN have been carried out attending to its properties, *i.e.* super basicity,[7-11] vibrational spectrum,[12] including theoretical[13] NMR spectroscopy (chemical shifts and spin-spin coupling constants),[14-18] and experimental X-ray diffraction studies.[19] Important reviews on naphthalene and related systems *peri*-substituted by group 15 and 16 elements have been published.[20, 21]

It was natural that the success of DMAN and its derivatives lead to study the effect of the replacement of the N atoms by other atoms of the same period 15, the pnicogen or pnictogen period, the contiguous ones being P and As. In particular, the field of compounds related to DMAN but with phosphorus instead of nitrogen atoms has been studied since their discovery in 1993 till today.[22-30]



DMAN

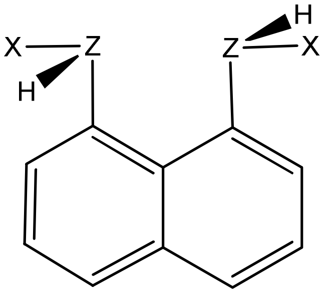
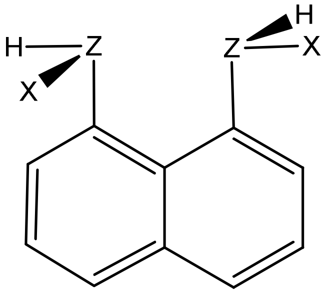
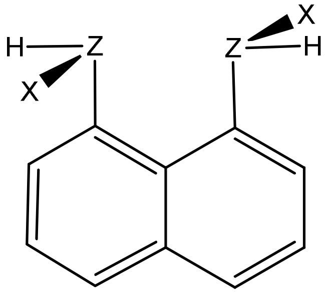


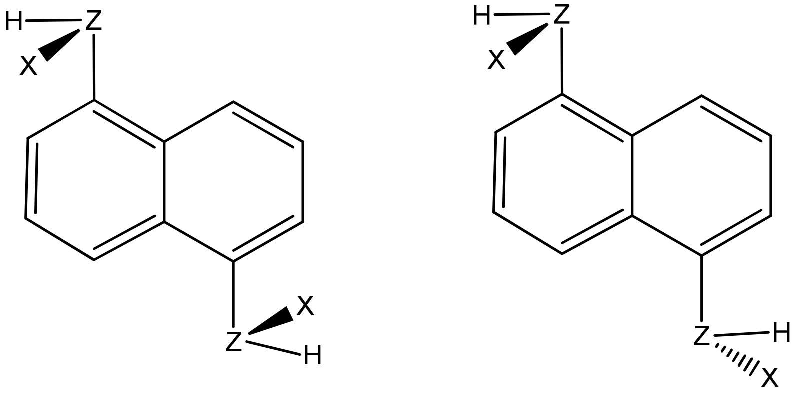
Numerous review articles have appeared devoted to the different aspects of the hydrogen bond that occurred between N atoms after proton trapping,[31-33] but, so far, there are no theoretical studies on pnicogen derivatives, with P and As instead of N atoms in structures type DMAN, and how is the intramolecular non-covalent interaction between the heteroatoms in absence of that proton. However, 1,8-bisphosphor naphthalene derivatives and its protonated structures have been experimentally studied.[21, 28, 34]

Non-covalent interactions are known to be responsible of the conformation of many molecules. Thus, the conformation of proteins is dominated by ionic interactions and hydrogen bonds. Other weak interactions as halogen bonds[35-37] and chalcogen bonds[38-43] can contribute to the stability of a given conformation. Pnicogen interactions[44-52] have been described in the literature, but, despite the fact that they have been known for several decades,[53-55] the pnicogen interaction did not attract much attention. In 2011, a remarkable publication of Hey-Hawking *et al.*[48] drew the attention of the scientific community to those bonds. The electrostatic nature of the pnicogen interactions has been rationalized based on the σ-hole concept [56-58] proposed by Politzer and Murray. The term σ-hole refers to the electron-deficient outer lobe of a p orbital involved in forming a covalent bond, especially when one of the atoms is highly electronegative. Thus, the pnicogen bonds shares with other non-covalent (weak) interactions the importance of the electrostatic interaction term.[59-70]

We have been extensively working on the description and analysis of the pnicogen interactions and acidic properties found in different complexes, both inter[71-82] and intramolecular ones.[83] Besides, other groups have published several articles in the field of pnicogen interactions including nitrogen, phosphorus, and arsenic atoms.[46, 75, 84-88]

In the present paper, we will report the results we obtained concerning the pnicogen interaction between P atoms and As atoms of 1,8-bis-substituted-naphthalene derivatives, analogues of the naphthalene proton sponges, with ZHX and ZX_2 as substituents, where Z = P, As, and X = H, F, Cl, and Br (Scheme 1). In ZHX compounds the phosphorus and arsenic atoms are stereogenic which results in the formation of (*R,S*) *meso* and (*R,R* and *S,S*) chiral isomers. For each compound, several conformations have been explored, including different X-Z···Z-X alignment, in which the X atoms are alignment with the P···P interaction axis, and the remaining substituents are located in both sides of the molecular plane which contains the naphthalene rings, at it was indicated in Scheme 1. The electron density shift of these compounds due to the pnicogen interaction has been characterized based on a partition scheme for non-bonding intramolecular interactions previously reported by us.[89]

		
1,8 XZ···ZX (*R,R*)	1,8 XZ···ZH (*R,S*)	1,8 HZ···ZH (*R,R*)

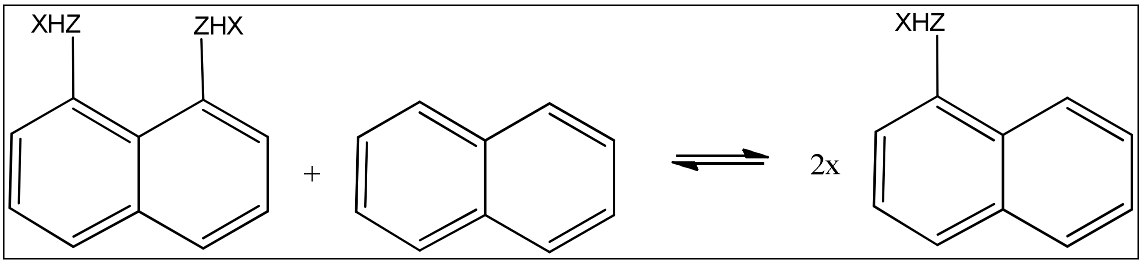


1,5 ZHX [C_2 (*R,R*) and C_i (*R,S*)]

Scheme 1. Different structures studied in this work.

2. COMPUTATIONAL DETAILS

The structures of the systems were optimized and characterized by frequency calculations at the MP2[90]/aug'-cc-pVDZ[91] computational level, which is a Dunning aug-cc-pVDZ[92, 93] with diffuse functions removed from the H atoms. In order to obtain more accurate interaction energies, single point MP2/aug'-cc-pVTZ calculations have been carried out over the MP2/aug'-cc-pVDZ optimized geometries. To avoid misleading nomenclature, the mentioned calculations will be named along the article as MP2/avdz and MP2/avtz, respectively. Calculations were performed using the Gaussian09 program.[94] The interaction energy (E_{iso}) between the pnicogen atoms has been obtained through isodesmic reaction as shown in Scheme 2.



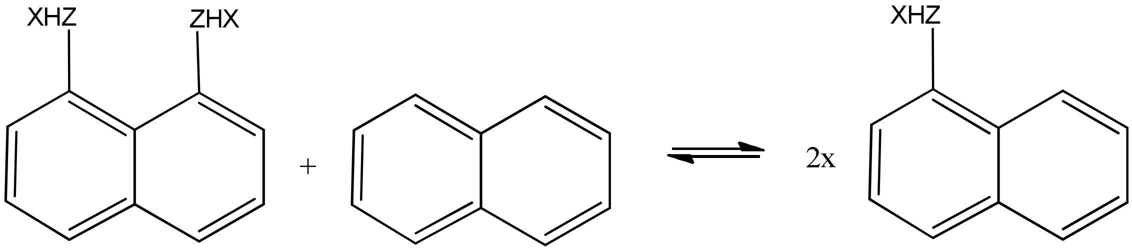
Scheme 2. Isodesmic reaction used to obtain the interaction energy.

The Atoms in Molecules (AIM) methodology[95, 96] was used to analyze the electron density of the systems with the AIMAll program.[97] The Natural Bond Orbital (NBO) method[98] has been employed to evaluate atomic charges using the NBO-3 program, and to analyze charge-transfer interactions between occupied and unoccupied orbitals.

The NCI (non covalent interactions) index, based on the reduced gradient of the electron density, has been calculated to identify attractive and repulsive interactions with the NCI program[99] and plotted with the VMD program.[100]

The intramolecular electron density shift (EDS) has been obtained using the fragmentation scheme proposed in ref. 89. This method proposes the calculation of the EDS of the intramolecular interaction by comparing the electron density of the interacting moieties substituted by hydrogen atoms as shown in Scheme 3. The EDS is calculated using Eq. 1

$$EDS = \rho_{AB} - \rho_{AH} - \rho_{HB} + \rho_{HH} \qquad \text{Eq. 1}$$



Scheme 3. Fragmentation scheme for the ZHX derivatives. An analogous fragmentation is used for the ZX_2 derivatives.

3. RESULTS AND DISCUSSION

3.1. Structure and Energy

The 1,8- and 1,5-bis-substituted (ZXH and ZX_2) systems have been studied including different pnicogen Z (Z = P and As) and halogen X (X = F, Cl, and Br) atoms. The stereogenic nature of some of the phosphine and arsine groups has been taken into account in the studied systems. In the case of 1,5-derivatives, we studied the *R,R* isomer with C_2 symmetry and the *R,S* one with C_i symmetry. In the 1,8-ones (ZXH), we have explored the meso form (*R,S*) and one of the two chiral forms (*R,R*) with different alignments of the substituents along the pnicogen interaction *i.e.* X-Z···Z-X (Scheme 1). Amongst all the possible arrangements, only three minima structures, for each X and Z, have been located: two in the chiral forms (X-Z···Z-X and H-Z···Z-H), and one in the meso isomer (X-Z···Z-H). All the attempts to optimize other conformations have reverted into the three mentioned ones, *e.g.*, the X-Z···Z-X (*R,S*) confirmation reverts into X-Z···Z-H (*R,S*) by rotation around the Z-C bond.

In order to get a compromise between the computational cost and methodology precision, we have performed a study of the basis set and methods used. We have selected a few systems (PH_2, PHF and PF_2 derivatives) and carried out geometry optimizations at MP2/avtz.

As it can be observed in Table S1, the differences between MP2/avdz and MP2/avtz in the P···P interatomic distances range from 0.05 to 0.08 Å, and within the dihedral angle formed by C-P···P-C, variation are less than 3º. The deformation out-of-plane of the PFH groups is almost constant with the different basis set considered. The differences in the distances are more disturbing, since it is a bit larger than expected.

Regarding the relative energy, E_{rel}, with respect to the 1,8-structure [X-Z···Z-X alignment in case of (*R,R*) ZHX compounds] and the interaction energy, E_{iso} (see Computational Details), have been compared using MP2/avdz and MP2/avtz optimized structures. Additionally, single point CCSD(T)/avdz and MP2/avtz calculations have been carried out over the MP2/avdz optimized structures in order to verify and analyze the effects on the interaction energies.

The data of Table S2 show that the interaction energies remain almost constant (±2 $kJ\cdot mol^{-1}$) in the PH_2 and PF_2 derivatives, both in relative energies and isodesmic energies. In the case of the PHF systems, the energies are more sensitive to the method and basis set used. In fact, CCSD(T) calculations show slightly smaller values than the MP2 method. In the case of the basis set, it can be seen that MP2 optimized energies aug-cc-pVDZ and aug-cc-pVTZ are slightly different, but MP2/avtz single point calculations over the MP2/avdz optimized geometries, give similar interaction and relative energies than those obtained from MP2/avtz optimizations. CCSD(T) calculations are very expensive, even for the smallest systems, and therefore unaffordable in the larger ones. On the other hand, MP2/avtz//MP2/avdz calculations present a good compromise between computational expenses and methodology precision, both in structure and interaction energies.

3.1.1. Structure

The interatomic pnicogen distances in the 1,8-bis-substituted naphthalene complexes have been gathered in Table 1. In the case of the phosphorus derivatives, they range between 2.62 and 3.04 Å, while in arsenic ones they vary from 2.82 to 3.13 Å. This variation is expected since the van der Waals radius of As is greater than P one, 1.85 and 1.80 Å, respectively.[101] In both series (phosphorus and arsenic derivatives), the 1,8-ZHBr system with Br-Z···Z-Br alignment is the one which presents the shortest interatomic distance. Comparing the pnicogen atom in the 1,8-ZXH series, As derivatives show in all the cases, longer interatomic distances than those found for P ones. Regarding the effect of the halogen substitution, there is a decrease in the Z···Z distance as the size of the halogen increases (F > Cl > Br), for analogous alignment. Amongst the three different alignment studied, the X-Z···Z-X is the one which presents the shortest distances, while the H-Z···Z-H shows the largest ones. The different possible alignments and their effect on the interatomic distance was previously studied for intermolecular P···P interactions on PH_2X dimers[71] where X-Z···Z-X was found to be the most favorable disposition with the strongest interaction.

The angle between X-Z···Z and X'-Z···Z, in which X and X' correspond to the atom with X-Z parallel and perpendicular to the Z···Z axis have been reported in Table1. As it can be observed, X-Z···Z angles range between 166-178º, confirming the parallel alignment of the interacting atoms, while X'-Z···Z ones vary between 84-99º, almost perpendicular to the Z···Z axis.

In addition, the angle formed by Z-C1-C2, in which C1 is the carbon atom bonded to the pnicogen, and C2 is the one connected with both benzene rings, has been measured and summarized in Table S3. The values range between 117 and 126º, and it has been found that the angle value correlates with the pnicogen interatomic distance, since the closer the angle, the shorter the Z···Z distance.

The dihedral angles formed between the C-Z···Z-C atoms are reported in Table S3. These angles can be used as a measure of the out-of-plane distortion experimented by the ZHX groups upon interaction. Comparing As and P compounds, the dihedral angle is not sensitive to the pnicogen atom, and remains almost constant when the comparison of similar families is done (i.e. PHF and AsHF). When the series of X_2 is considered, the dihedral angle becomes wider with the size of the X, H < F < Cl < Br. It is also consistent with the interatomic distance between the pnicogen atoms, the shorter the distance, the larger the dihedral angle. Across the ZHX series, comparing those compound with the same alignment, X-Z···Z-X dihedral angles evolves from X=F (narrowest) to Br (widest), but the range is less than 4°. Something similar occurs for the angles in compounds with X-Z···Z-H alignment. Surprisingly, this does not happen with the H-Z···Z-H alignment, since the widest angle is found in fluorine derivatives. Additionally, in these dispositions the dihedral angle does not correlate with the interatomic distances.

For each ZHX family, the out-of-plane distortion is larger in those compound with X-Z···Z-X alignment, and smallest in the H-Z···Z-H one, being intermediate in the X-Z···Z-H alignment.

Table 1. Relative energies (E_{rel}, kJ·mol^{-1}), isodesmic energies (E_{iso}, kJ·mol^{-1}), interatomic distance between the pnicogen atoms (R, Å) and X-Z···Z angles (°) of the systems studied at MP2/avtz//MP2/avdz computational level.

System and alignment		Sym	E_{rel}[a]	E_{iso}	R	X-Z···Z[b]	X'-Z···Z[c]			Sym	E_{rel}[a]	E_{iso}	R	X-Z···Z[b]	X'-Z···Z[c]
1,8-PHF								1,8-AsHF							
FP···PF	*R,R*	C_2	0.0	-13.5	2.68	166.9	96.4	FAs···AsF	*R,R*	C_2	0.0	-7.1	2.88	167.4	98.5
FP···PH	*R,S*	C_1	11.0	-1.3	2.81	178.5(164.2)[d]	97.4(84.5)[d]	FAs···AsH	*R,S*	C_1	6.8	-0.2	2.95	174.5(166.7)[d]	98.0(83.5)[d]
HP···PH	*R,R*	C_2	28.1	17.0	2.98	176.7	87.0	HAs···AsH	*R,R*	C_2	21.6	14.6	3.08	173.7	84.[illegible]
1,5-PHF	*R,R*	C_2	12.7	1.6				1,5-AsHF	*R,R*	C_2	8.9	1.8			
	R,S	C_i	12.7	1.6					*R,S*	C_i	8.4	1.4			
1,8-PHCl								1,8-AsHCl							
ClP···PCl	*R,R*	C_2	0.0	-6.3	2.67	166.0	96.8	ClAs···AsCl	*R,R*	C_2	0.0	-5.3	2.84	166.6	98.8
ClP···PH	*R,S*	C_1	11.1	9.8	2.84	174.8(169.3)[d]	95.2(88.6)[d]	ClAs···AsH	*R,S*	C_1	8.1	7.6	2.96	177.2(171.8)[d]	94.3(89.0)[d]
HP···PH	*R,R*	C_2	12.7	16.5	2.99	176.2	88.5	HAs···AsH	*R,R*	C_2	8.4	12.6	3.08	174.3	85.7
1,5-PHCl	*R,R*	C_2	–2.0	1.7				1,5-AsHCl	*R,R*	C_2	-2.4	1.8			
	R,S	C_i	–2.2	1.6					*R,S*	C_i	-2.9	1.3			
1,8-PHBr								1,8-AsHBr							
BrP···PBr	*R,R*	C_2	0.0	-10.9	2.62	165.1	97.4	BrAs···AsBr	*R,R*	C_2	0.0	-8.4	2.82	166.1	99.1

BrP···PH	*R,S*	C_1	13.1	9.4	2.84	172.7(170.6)[d]	94.5(90.8)[d]	BrAs···AsH	*R,S*	C_1	9.1	7.5	2.96	174.7(172.7)[d]	93.6(91.5)[d]
HP···PH	*R,R*	C_2	10.0	13.6	2.98	176.5	87.9	HAs···AsH	*R,R*	C_2	3.7	9.0	3.08	173.9	85.3
1,5-PHBr	*R,R*	C_2	–2.1	1.6				1,5-AsHBr	*R,R*	C_2	-4.1	1.1			
	R,S	C_i	–2.6	1.1					*R,S*	C_i	-4.5	0.8			
1,8-PH_2	-	C_2	0.0	21.2	3.04	176.5	84.8	1,8-AsH2	-	C_2	0.0	20.2	3.13	173.9	86.5
1,5-PH_2	-	C_2	-20.6	0.6				1,5-AsH2	-	C_2	-20.1	0.1			
	-	C_i	-20.6	0.6					-	C_i	-20.1	0.1			
1,8-PF_2	-	C_1	0.0	13.0		168.2	96.2	1,8-AsF_2	-	C_1	0.0	13.5	3.11	169.9	95.1
1,5-PF_2	-	C_2	-9.6	3.4				1,5-AsF_2	-	C_2	-10.0	3.6			
	-	C_i	-9.8	3.2					-	C_2	-9.4	4.2			
1,8-PCl_2	-	C_2	0.0	8.9		161.8	98.2	1,8-$AsCl_2$	-	C_2	0.0	9.6	2.99	161.8	98.2
1,5-PCl_2	-	C_2	-5.1	3.9				1,5-$AsCl_2$	-	C_2	13.7	4.1			
	-	C_i	-5.4	3.6					-	C_i	13.1	3.5			
1,8-PBr_2	-	C_2	0.0	2.6		160.5	98.3	1,8-$AsBr_2$	-	C_2	0.0	2.3	2.92	162.2	98.4
1,5-PBr_2	-	C_2	5.5	2.9				1,5-$AsBr_2$	-	C_2	5.2	2.9			
	-	C_i	5.5	3.0					-	C_i	5.0	2.6			

[a] Relative energy obtained as a difference with respect to the 1,8-structure. In the case of ZHX compounds, the relative energy is respect to the 1,8-structure with X-Z···Z-X alignment

[b] Angle correspond to that formed by X-Z···Z, with linear alignment.

[c] Angle correspond to that formed by X-Z···Z, with X-Z perpendicular to the Z···Z axis.

[d] Number in parenthesis correspond to the angles in the group with Z-H.

3.1.2. Energy

Table 1 shows the relative energies of the different compounds with respect to the 1,8-structure (X-Z···Z-X alignment in case of (*R,R*) ZHX compounds). The relative energies show that in PX_2 and PHX systems, the 1,5-bis-substituted derivatives are in all cases more stable than the 1,8- ones, with the exception of the PHF and PBr_2 derivatives. In the case of AsX_2, 1,8-derivatives are more stable than 1,5-ones for Cl and Br, and the opposite is true for AsH_2 and AsF_2 systems. Considering the different alignments within ZHX systems, X-Z···Z-X alignment is always the most stable one for both Z = P and As, followed by the X-Z···Z-H one, being the H-Z···Z-H the least stable one, with the exception of the ZHBr derivatives in which the H-Z···Z-H alignment is slightly more stable than the X-Z···Z-H one.

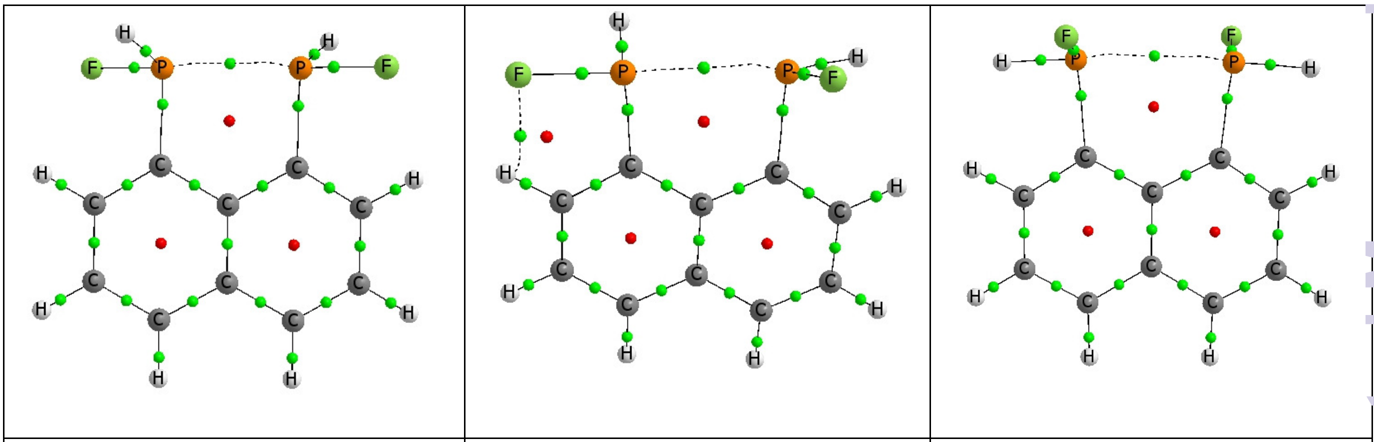
The interaction energy (E_{iso}) between the pnicogen atoms has been obtained through isodesmic reaction (Scheme 2), and gathered in Table 1. In addition to the 1,8-derivatives, the interaction energies of the 1,5-ones have been obtained. Since the interaction energy in 1,5-compounds should be 0, the E_{iso} value obtained can be used as an indicator of how reliable is the isodesmic reaction approach.

Regarding the interaction energy, E_{iso}, the 1,8-compounds with XZ···ZX alignment present negative values of E_{iso}, meaning that the compound which presents Z···Z interaction is more stable than the molecules without it, and therefore, the attractive pnicogen interaction compensates the remaining steric repulsions. Same features were found for the FZ···ZH alignment in both P an As derivatives. The remaining complexes show interaction energies with positive values. The fact that negative values are present on the XZ···ZX alignment compounds is coherent with those being the ones with the shortest Z···Z distances.

Considering the same alignment in ZHX complexes, the evolution of the E_{iso} across the halogen series is F < Br < Cl, with the exception of the HZ···ZH ones, in which a F < Cl < Br variation is found. Similar features are shown by ZX_2 complexes in which, the E_{iso} and the pnicogen interatomic distance evolve in the same way, the shorter the distance, the smaller the interaction energy. However, the evolution of the E_{iso} respect to the halogen substituent is F > Cl > Br. The addition of a second halogen withdraws density from the pnicogen lone pair, and therefore, its electron donation capacity is reduced, having a weaker effect on the interaction.[48]

3.2. Electronic properties (AIM, NBO, EDS, NCI)

In all structures considered for the 1,8-bis-substituted derivatives (26 cases in total), intramolecular pnicogen interactions have been found, characterized by a Bond Critical Point (BCP) between the interacting atoms (see Figure 1 and S1). The electron density (ρ) on the BCP ranges from 0.019 to 0.049 a.u. In phosphorus derivatives, the range of ρ is slightly wider (0.019-0.049) than in the arsenic ones (0.019-0.038). Laplacian ($\nabla^2\rho$) values from 0.028 to 0.046 a.u. suggest closed shell regimen interactions, being this range wider in P derivatives (0.028-0.046 au) than in As ones (0.035-0.042 au). The nature of the pnicogen bonds have been characterized based on the value at the bond critical point of the Laplacian, C ratio ($C = |V|/G$, where V and G are the electron potential and kinetic energy densities, respectively)[102] and H, the total electron density energy ($H = V+G$).[103] Based on the positive values of the Laplacian (Table 2), C values between 1 and 2 and negative values of H (Table S4), the pnicogen interactions found here can be classified as pure closed shell interactions with a partial covalent character.



1,8-PHF FP···PF (*R*,*R*) | 1,8-PHF FP···PH (*R*,*S*) | 1,8-PHF HP···PH (*R*,*R*)

Figure 1. Molecular graphs for some examples of the systems studied 1,8-PHF with different alignments. Green and red dots indicate bond critical (BCP) and ring critical (RCP) points.

Table 2. Electron density (ρ), Laplacian ($\nabla^2\rho$), and interatomic distance (R, Å) at MP2/aug'-cc-pVDZ computational level.

System and alignment		ρ	$\nabla^2\rho$	System and alignment		ρ	$\nabla^2\rho$
1,8-PHF				1,8-AsHF			
FP···PF	*R,R*	0.043	0.034	FAs···AsF	*R,R*	0.032	0.037
FP···PH	*R,S*	0.033	0.044	FAs···AsH	*R,S*	0.028	0.042
HP···PH	*R,R*	0.023	0.043	HAs···AsH	*R,R*	0.021	0.039
1,8-PHCl				1,8-AsHCl			
ClP···PCl	*R,R*	0.044	0.033	ClAs···AsCl	*R,R*	0.036	0.036
ClP···PH	*R,S*	0.031	0.044	ClAs···AsH	*R,S*	0.028	0.041
HP···PH	*R,R*	0.024	0.045	HAs···AsH	*R,R*	0.022	0.041
1,8-PHBr				1,8-AsHBr			
BrP···PBr	*R,R*	0.049	0.028	BrAs···AsBr	*R,R*	0.038	0.035
BrP···PH	*R,S*	0.031	0.045	BrAs···AsH	*R,S*	0.028	0.041
HP···PH	*R,R*	0.024	0.046	HAs···AsH	*R,R*	0.022	0.042
1,8-PH_2	-	0.019	0.041	1,8-AsH_2	-	0.019	0.038
1,8-PF_2	-	0.023	0.042	1,8-AsF_2	-	0.020	0.036
1,8-PCl_2	-	0.032	0.045	1,8-$AsCl_2$	-	0.027	0.039

1,8-PBr_2	-	0.038	0.043	1,8-$AsBr_2$	-	0.031	0.039

Exponential relationships have been found between the electron density at the BCP and the corresponding interatomic distance (Fig. 2). Similar relationships have been described for other weak interactions.[42, 80, 83, 102, 104-111]

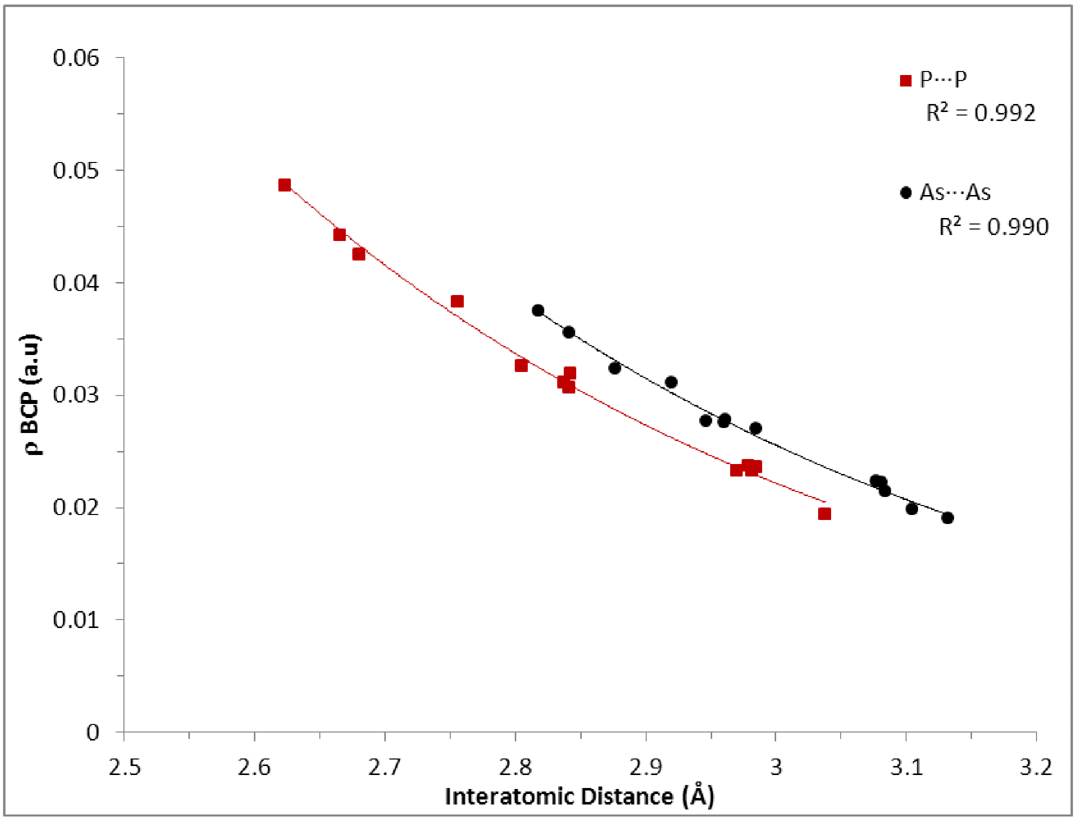
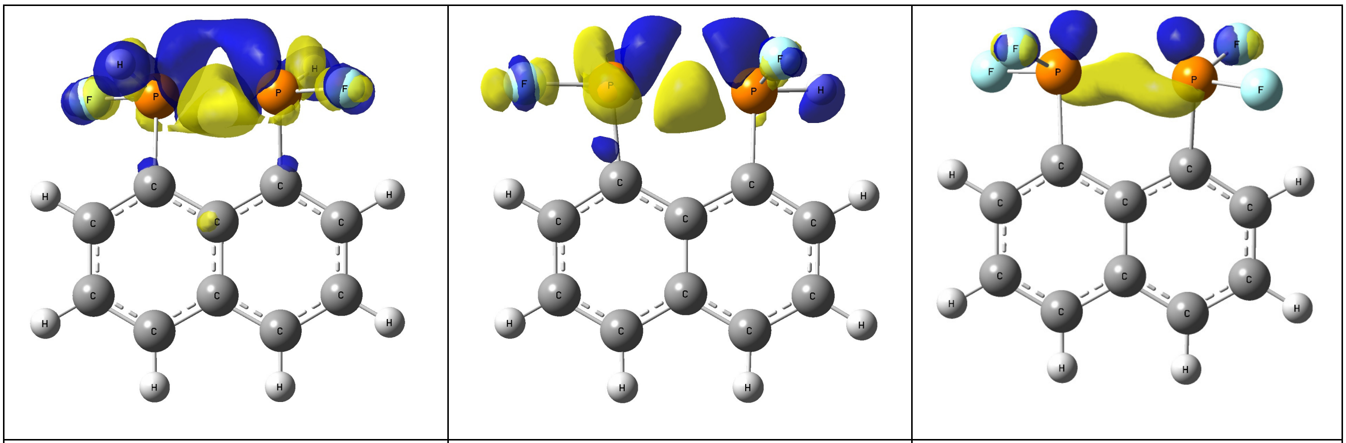


Figure 2. Relationship between the interatomic distance (Å) and the value of the electron density at BCP (a.u.) for P···P and As···As interactions.

The electron density shift maps (EDS) of the intramolecular interactions have been obtained following the procedure reported in ref. 89 and depicted in Figure 3. Blue and yellow areas correspond to those with a decrease and an increase of the electron density, respectively. A large area with positive values of the EDS is found in the region between both pnicogen atoms, corresponding to an increase of the electron density respect to the non interacting systems. This pattern was already found for other intramolecular pnicogen interactions.[83] For example, the PHF derivative with FP···PF alignment shows larger ρ in the BCP than the FP···PH one, in parallel to the increment of electron density in the interaction region as shown in Figure 3. The fact that XZ···ZX alignments present higher values of the electron density at the BCP than HZ···ZH is coherent with the more positive values of the σ-hole generated by the halogens along the X-P and X-As axis than along H-Z.[112, 113]



1,8-PHF FPPF (*R*,*R*) | 1,8-PHF FPPH (*R*,*S*) | 1,8-PF_2

Figure 3. Electron Density Shifts at 0.001 au of some of the PHF complexes at MP2/aug'-cc-pVDZ computational level. Blue and yellow surfaces indicate the lost and gain of electron density, respectively.

In addition, non-covalent index plots for two representative compounds have been obtained. As it can be seen in Fig. S2, a blue-green area appears between the interacting atoms in the complexes. Those blue-green areas correspond to an attractive and weak interaction with $\lambda_2 \approx 0$, which is in agreement with the AIM analysis.

We have computed the charge in the pnicogen atoms by means of AIM charges and NBO second order energies. In Table S5, the net charge associated to atoms Z, X, and H belonging to ZXH groups, and the total sum of the group are reported. In addition, the variation of the charge on the pnicogen atoms of the 1,8-bis-substituted derivatives with respect to the corresponding monosubstituted derivatives is gathered in Table 3.

Except in a few cases (mostly in HZ···ZH alignment systems), the variation of total charge on the pnicogen atom is negative respect to the mono-substituted derivatives, meaning an increase of charge on the P and As atoms respect to the mono-substituted compound. Those cases with $\Delta Q \approx 0$ indicate an extremely weak interaction between the pnicogen atoms. This fact is also corroborated by the NBO data in which there is a small donation from the pnicogen lone pair to the antibonding σ^*Z-X (-H) orbital. However, no correlation was found between the charge difference on pnicogen atom and the NBO transfer.

In addition, the change in the total charge associated to the ZHX and ZX_2 groups, ΔQ_{net} (ZHX)[a], has been examined. The difference between ΔQ_{net} (Z) and ΔQ_{net} (ZHX) can be used to estimate the effect of the substituents on the charge transferred. In general, ΔQ_{net} (ZHX) follows the same trend that ΔQ_{net} (Z) which is consistent with the idea that the most important atom, and therefore the one which suffers more change in the net charge, is the pnicogen one. However, in some cases which involve asymmetrical alignment (X-Z···Z-H), the pnicogen atoms show negative increments of the charge (*e.g.* F-As···As-H), despite that the opposite would be expected. The situation changes dramatically, when the ΔQ_{net} of the whole group is taken into account. As it can be observed, those cases present positive variation, in other words, an increment on the charge, consistent with the situation in which X-Z groups donates more charge into the Z-H rather than the other way around.

The NBO analysis of the pnicogen bond shows electron donation from the lone pair of one Z1 to the antibonding orbital σ*Z2-X (see Fig. 5). Regarding the NBO E(2) energies, P derivatives show higher values of donation from LP P1→σ*P2-X than in the As ones. In the cases of asymmetric alignment, both donation from Z1→σ*Z2-X and Z1→σ*Z1-H have been considered, finding, as expected, that the former is larger than the latter. As a general rule, the orbital energy transfer is larger in those compounds with shorter pnicogen···pnicogen distances. In fact, quadratic relationships have been found between those magnitudes (Fig. 6) with r^2 = 0.99 and 0.98, corresponding to P and As derivatives, respectively.

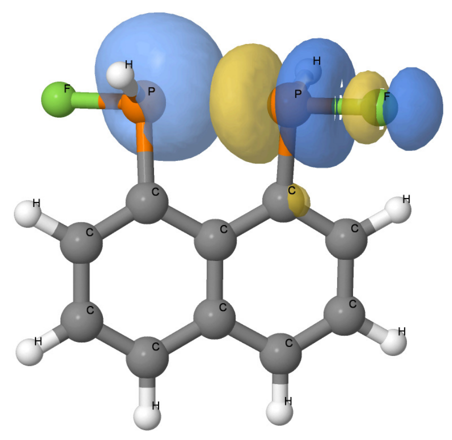
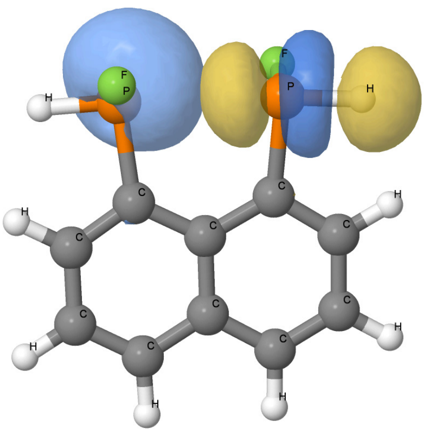
	
1,8-PHF FP···PF (*R,R*)	1,8-PHF HP···PH (*R,R*)

Figure 5. Orbital representation corresponding to the donation from LP P1 to σ*P2-X (-H). Left and right, 1,8-FP···PF and 1,8-HP···PH derivatives respectively. Left light blue lobe corresponds to the electron lone pair belonged to P1 atom. Yellow-Blue pattern corresponds to antibonding P2-X(-H) orbital.

Table 3 Charge difference on pnicogen atom ZHX and ZX_2 groups ($\Delta Q_{net,}$ e), and NBO E(2) orbital interaction energies ($kJ \cdot mol^{-1}$) at B3LYP/aug'-cc-pVDZ computational level.

	E(2)					E(2)			
	LP P1→ σ*P2-X	LP P2→ σ*P1-H	ΔQ_{net} (P)[a]	ΔQ_{net} (PHX)[a]		LP As1→ σ*As2-X	LPAs2→ σ*As1-H	ΔQ_{net} (As)[a]	ΔQ_{net} (AsHX)[a]
1,8-PHF					1,8-AsHF				
FP···PF	75.0		–0.012	–0.011	FAs···AsF	60.7		–0.032	–0.015
FP···PH	67.6	22.8	–0.045 (0.023)[b]	–0.051 (0.036)	FAs···AsH	62.5	22.4	–0.030 (–0.010)[b]	–0.030 (0.018)[c]
HP···PH		19.1	-0.001	–0.002	HAs···AsH		19.0	0.007	0.006
1,8-PHCl					1,8-AsHCl				
ClP···PCl	78.6		–0.029	–0.019	ClAs···AsCl	67.4		–0.031	–0.013
ClP···PH	53.9	26.9	–0.037 (0.008)[b]	–0.038 (0.012)[c]	ClAs···AsH	54.	28.0	–0.014 (–0.019)[b]	–0.012 (0.008)[c]
HP···PH		20.0	–0.004	–0.004	HAs···AsH		21.5	0.004	0.004
1,8-PHBr					1,8-AsHBr				
BrP···PBr	89.4		–0.024	–0.022	BrAs···AsBr	71.5		–0.030	–0.014
BrP···PH	53.1	28.9	–0.032 (–0.009)[b]	–0.037 (0.007)[c]	BrAs···AsH	52.3	29.6	–0.010 (–0.025)[b]	–0.009 (0.005)[c]
HP···PH		20.8	–0.008	–0.003	HAs···AsH		22.3	0.000	–0.105
1,8-PH$_2$	18.6		–0.011	–0.017	1,8-AsH$_2$	21.5		–0.001	–0.002
1,8-PF$_2$	23.7		–0.006	–0.006	1,8-AsF$_2$	21.8		–0.010	–0.004
1,8-PCl$_2$	40.7		–0.016	–0.006	1,8-AsCl$_2$	37.2		–0.015	–0.002
1,8-PBr$_2$	54.1		–0.024	–0.008	1,8-AsBr$_2$	46.6		–0.020	–0.003

[a] Charge difference respect to the monosubstituted derivative.

[b] Values in parenthesis corresponds to the P (As) atoms with P-H (As-H) alignment .

[c] Values in parenthesis corresponds to the ZHX groups with Z-H (Z-H) alignment .

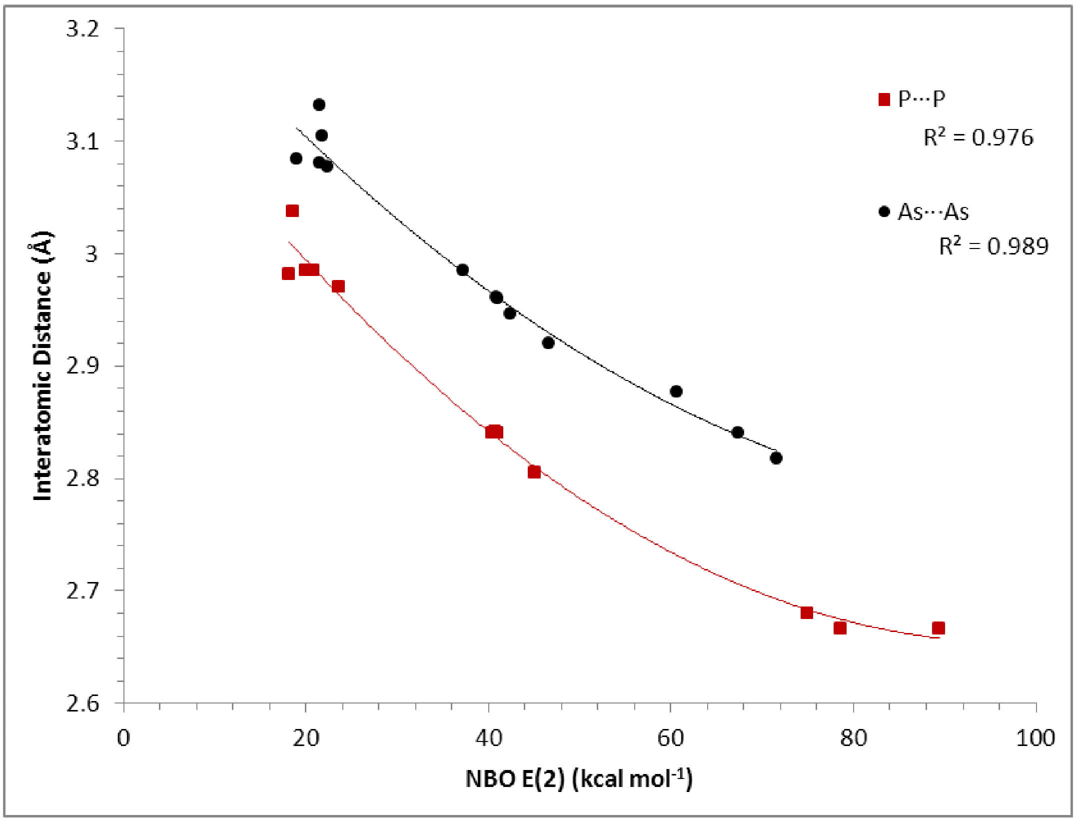


Figure 6. Relationship between the interatomic distance (Å) and the second order interaction energy, E(2) for P···P and As···As interactions

3.3. CSD search

A search in the CSD for 1,8-bis-phosphines, without the presence of metals in the crystal structure, provide fourteen hits which include those with 1,8-PH_2, 1,8-PCl_2 and 1,8-PBr_2 already reported in the present study. In contrast, no 1,8-bis-arsine derivatives are found in the CSD. Eleven of the hits can be classified as $(PX_2)_2$, two of them are $(PXY)_2$ and one case is $(PX_2)(PY_2)$. A complete list of the CSD refcodes with some of their geometrical parameters is given in the SI.

A total of 21 P···P intramolecular distances can be identified in the 14 hits found, ranging from 2.77 to 3.27 Å. The shortest distance corresponds to the refcode GUTJIO compound, which is the 1,8-PBr_2 derivative. The calculated geometrical parameters associated to the P···P interaction, for the three systems calculated and present in the CSD search, are in reasonably good agreement with those found in the crystal structures taking into account that the calculations are carried out in the gas phase while the experimental structures include the packing effects (Table 4 and S6). For comparative purposes, the structures of two small systems found in the CSD have been calculated, the tetramethyl and tetramethoxy derivatives. As in the case of the halogen derivatives, the agreement between the calculated and experimental values is very good (Table 4).

Table 4. Comparison of the calculated and experimental (in parenthesis) geometrical parameters (Å and º) of the three 1,8-bis-phosphine derivatives studied in the present and found in the CSD database.

Der.	CSD Refcode	P···P	P-C-C	C-Z··Z-C
PH_2	FAKQAK	3.038 (2.985)	123.5 (123.8)	17.8 (1.3)
PCl_2	GUTJEK	2.842 (2.798/2.811)	118.3 (118.5/119.4)	32.6 (23.5/20.5)
PBr_2	GUTJIO	2.758 (2.767)	117.2 (116.8)	33.1 (33.9)
PMe_2	RESNUY	3.011 (3.036/3.070)	120.9 (123.1/121.6)	28.7 (16.9/25.8)
P(OMe)2	ULIJAA	2.955 (2.912)	122.0 (121.8)	19.2 (11.4)

As expected, the representation of the P···P interatomic distance *vs*. the P-C-C angle (Fig. S3) shows an almost linear behavior for those cases with interatomic distances shorter than 3.0 Å, while for longer distances the values are scattered. The scatter values for longer distances that 3.0 Å could indicate that the pnicogen interaction is perturbed by other interactions in the crystal structure.

CONCLUSIONS

We have reported a detailed study of the proton sponges analogues and its intramolecular pnicogen interactions found in 1,8-ZXH and 1,8-ZX_2 bis-substituted naphthalene derivatives, attending at their structural, energetic and electronic properties. Our findings can be summarized as follows:

- The pnicogen interacting distance shows similar ranges than those found for intermolecular pnicogen systems [*e.g.* $(PHFX)_2$ homodimers], varying between 2.62-3.04 Å, and 2.82-3.13 Å for phosphor and arsenic derivatives, respectively. The Z-C-C angles (117-126º) and out-of-plane dihedral angles (2-34º) have been evaluated in order to give an insight of the distortion upon interaction.
- The interaction energy, E_{iso}, has been obtained through isodesmic reactions. Negative values of E_{iso} have been found for 1,8-XZ···ZX and 1,8-FZ····ZH compounds, while in the remaining ones it present positive values, indicating than the pnicogen interaction does not compensate the steric impediments.
- Electron density analysis of the pnicogen interactions has been carried out by means of AIM analysis. Exponential relationships between interatomic distance and electron density at the

BCP have been found. Electron density shift maps and NCI plots have been used as graphical tools to support the analysis findings.

- Orbital interaction energies, E(2), from NBO analysis have been obtained to elucidate the charge transferred from the lone pair belonging to the pnicogen atom to the antibonding Z-X and Z-H orbital. The E(2) values range from 18.6 to 89.4 kJ·mol^{-1} and correlate exponentially with the interatomic Z···Z distances.
- A search on the CSD has been carried out in order to compare our results with X-ray crystallographic data. Experimental intramolecular P···P distances from the CSD have been shown to be in close agreement with the intramolecular calculated distances between the pnicogen atoms.

Supporting Information

The Supporting Information includes structural distances for MP2 comparison at different basis set, and MP2 and CCSD(T) calculations benchmark for selected examples, angles, electron density properties, AIM charges and molecular graphs for all compound studied, and NCI plots for representative compounds. Additionally, 1,8-bis-phosphine derivatives found in the CSD database with some of their geometrical characteristics, including graphs of P···P distances versus P-C-C angles. The material is available free of charge via the Internet at doi:

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