

On the Reliability of Pure and Hybrid DFT Methods for the Evaluation of Halogen, Chalcogen, and Pnicogen Bonds Involving Anionic and Neutral Electron Donors

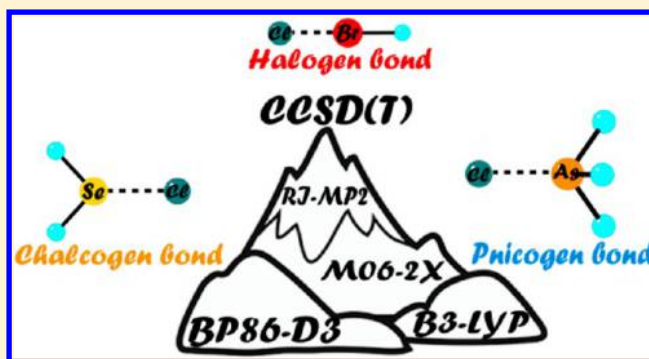
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S Supporting Information

ABSTRACT: In this article, we report a comprehensive theoretical study of halogen, chalcogen, and pnicogen bonding interactions using a large set of pure and hybrid functionals and some ab initio methods. We have observed that the pure and some hybrid functionals largely overestimate the interaction energies when the donor atom is anionic (Cl^- or Br^-), especially in the halogen bonding complexes. To evaluate the reliability of the different DFT (BP86, BP86-D3, BLYP, BLYP-D3, B3LYP, B97-D, B97-D3, PBE0, HSE06, APFD, and M06-2X) and ab initio (MP2, RI-MP2, and HF) methods, we have compared the binding energies and equilibrium distances to those obtained using the CCSD(T)/aug-cc-pVTZ level of theory, as reference. The addition of the latest available correction for dispersion (D3) to pure functionals is not recommended for the calculation of halogen, chalcogen, and pnicogen complexes with anions, since it further contributes to the overestimation of the binding energies. In addition, in chalcogen bonding interactions, we have studied how the hybridization of the chalcogen atom influences the interaction energies.



1. INTRODUCTION

Noncovalent bonding interactions play a major role in many chemical and biological phenomena, and consequently, they have been intensively investigated for many years.¹ The strength of these interactions varies from weak van der Waals forces between nonpolar entities to strong electrostatic ion–ion attractions.² Probably the most studied and analyzed noncovalent interaction is the hydrogen bond ($\text{AH}\cdots\text{D}$, A refers to the electron acceptor and D to the donor), where A can be basically any atom more electronegative than H and D can be any entity with the ability to act as an electron donor (lone pair, π -system, anion, etc.).³ Among many interactions, those involving halogen, chalcogen, and pnicogen atoms have attracted considerable attention in recent years, and they are increasingly being recognized by scientists and used in supramolecular chemistry, crystal engineering, and biochemistry.⁴

Halogen bonding (XB) is usually defined as a moderately strong and directional noncovalent interaction of an electro-positive halogen ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) and an electron donor species (D).^{5,6} In the general description $\text{Y}-\text{X}\cdots\text{D}$,⁵ the Lewis base (neutral or anionic) gives electron density to the acceptor X (Lewis acid), which is covalently attached to atom Y (usually C, N, or O). The $\text{Y}-\text{X}\cdots\text{D}$ angle is nearly lineal, and the distance between the halogen bonding donor and acceptor atoms ($\text{X}\cdots\text{D}$) is shorter than the sum of their van der Waals

radii. The pioneering work on XB interactions is attributed to Guthrie,⁷ and numerous years later were further studied by Hassel.⁸ However, the interest for this noncovalent interaction has enormously grown after its recent renaissance.⁹ It has been broadly studied both experimentally and theoretically.¹⁰ A very interesting example is the exceptionally short carbon–chlorine bond in chlorotrinitromethane (1.694 Å), which is explained by means of three simultaneous $\text{O}\cdots\text{Cl}$ halogen bonds.¹¹ The applications of the halogen bonding interaction extend from supramolecular chemistry¹² and crystal engineering^{5,13} to polymer sciences,¹⁴ liquid crystals,¹⁵ and conductive materials.¹⁶ Moreover, it is gradually studied and analyzed in medicinal chemistry^{13,17} and biological systems.¹⁸

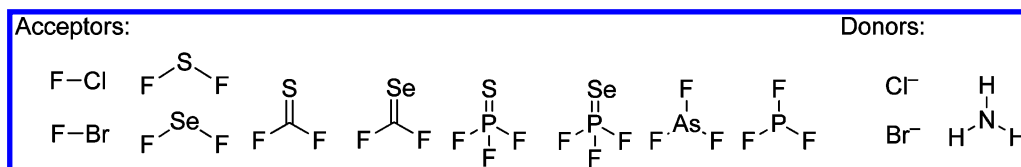
Similar to halogen atoms, the heavier chalcogen atoms (Se, Te, Po) also have a localized positive region on the extension of the covalent bonds (σ -hole). Therefore, the chalcogen atom (Ch) is able to interact favorably with an electron donor (D) to form a noncovalent interaction, which is similar in nature to the halogen bond, namely, $\text{Y}-\text{Ch}\cdots\text{D}$. The well-recognized chalcogen bond frequently refers to the noncovalent chalcogen–chalcogen interaction,¹⁹ in which the donor (D) atom is also a chalcogen, similar to the halogen–halogen interaction. Some interesting works were devoted to the study of

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Scheme 1. Electron Donors and Acceptors Studied in This Article



chalcogen–chalcogen interactions. For instance, Iwaoka et al.²⁰ have suggested that S...O interactions stabilize folded protein structures. Moreover, Bleiholder et al.²¹ have examined a large set of model systems to understand the intermolecular interactions between chalcogen centers. Obviously, apart from chalcogen atoms, the electron donor can be another atom or group.²² For instance, sulfur– π contacts are also important chalcogen bonds, as demonstrated by Reid et al. using CSD searches,²³ which have been the subject of many theoretical studies due to their importance in biological systems.²⁴ Finally, analogously to halogen and chalcogen bonds, a pnictogen bond (also denoted as pnictogen) arises when the acceptor is an element of group 15 of the periodic table (pnictide family). This interaction has been defined as a new supramolecular linker²⁵ and has been recently analyzed in terms of its energetic nature, effects of the substituents, and sensitivity of angular distortion.²⁶ The NMR characteristics (chemical shieldings and nuclear–nuclear coupling constants) have been explored theoretically for a number of complexes.^{27,28} Pnictogen bonds show a high degree of anisotropy, and distortions of pnictogen bonds away from their preferred geometry cause a more rapid loss of stability than in H-bonds. Moreover, the favorable interaction of arenes with heavier pnictogens (E = As, Sb, and Bi) has also been known for a long time, but its study in the context of supramolecular chemistry has been expanded more recently.²⁹ The extensive work developed by Johnson's group in the last years emphasizes the potential use of this interaction to control self-assembly processes that yield the formation of macrocycles.³⁰ In addition, it has been demonstrated that the pnictogen– π interaction is relevant in biological systems since it likely participates in the mechanism of inhibition of Sb-based drugs used to treat leishmaniasis.³¹ Finally, there are some comparative studies of the four interactions that have been published related to the concept of σ -holes.^{32,33}

The appropriate theoretical description of these interactions is of paramount importance for either understanding chemical and biological processes or designing new compounds able to accomplish a given function based on halogen, chalcogen, or pnictogen interactions. In this respect, density functional theory (DFT) calculations have become a vital tool in the research on a variety of physical, chemical, and material science problems. However, there are many DFT methods (pure, hybrid, dispersion-corrected, etc.) that may make the adequate choice for dealing with a given noncovalent interaction difficult. In this article, we report an extensive theoretical study where we analyze the reliability of the most commonly used DFT methods (with and without dispersion correction), and ab initio HF, MP2, and RI-MP2 methods by comparing the energies and equilibrium distances with the reference values computed at the CCSD(T)/aug-cc-pVTZ level of theory in model halogen, chalcogen, and pnictogen complexes using two types of donor atoms (anions and ammonia; see Scheme 1).

2. COMPUTATIONAL METHODS

The geometry of the monomers and complexes studied in this article has been fully optimized at several DFT (BP86,³⁴ BP86-D3,³⁵ BLYP,³⁴ BLYP-D3,³⁶ B3LYP,³⁷ B97-D,³⁸ B97-D3,³⁹ PBE0,⁴⁰ HSE06,⁴¹ APFD,⁴² and M06-2X⁴³) and ab initio methods [MP2,⁴⁴ RI-MP2,⁴⁵ and CCSD(T)⁴⁶] and the Dunning type aug-cc-pVTZ basis set.⁴⁷ Frequency calculations have been carried out at the same computational level to confirm that the obtained structures correspond to energetic minima. The calculations were performed using the Gaussian 09⁴⁸ and Turbomole 6.5⁴⁹ programs. The binding energies were calculated as differences between the energy of the complex and the sum of energies of monomers optimized separately. Hence, the effect of the deformation connected with the complexation was included in the binding energies.

The potential error due to the BSSE correction has been considered by means of the counterpoise method. The correction in the case of the DFT methods is always smaller than 3.6 kJ/mol, whereas it is more important with the MP2, RI-MP2, and CCSD(T) methods, but it is known that the counterpoise methodology overestimated the correction in these computational methods.⁵⁰ However, the inclusion of the correction does not change significantly the results obtained without BSSE, and thus, the discussion along the text is carried out in the uncorrected energy values. For those readers interested in a comparison of the corrected and uncorrected interaction energies, their values have been gathered in the Supporting Information.

To analyze statistically the data, the CCSD(T)/aug-cc-pVTZ results have been used as reference. Initially, linear correlations have been carried out between the DFT and ab initio results and the reference ones. The values of the intercept, slope, and square correlation coefficients of those correlations have been considered. The best methods should provide values close to zero, one, and one, respectively. In addition, two estimations of the error have been taken into account: the average absolute error AAE (eq 1) and the mean absolute percentage error MAPE (eq 2)

$$AAE_i = \frac{1}{n} \sum_{j=1}^n |E_j(i) - E_j[\text{CCSD(T)}]| \quad (1)$$

$$\text{MAPE}_i = 100 * \frac{1}{n} \sum_{j=1}^n \frac{|E_j(i) - E_j[\text{CCSD(T)}]|}{|E_j[\text{CCSD(T)}]|} \quad (2)$$

where $E_j(i)$ is the value of the interaction energy of complex j with method i .

The main difference between the information provided by the AAE and MAPE parameters is that the latter penalizes more than the former the error in those cases with smaller interaction energies in the reference method.

The molecular electrostatic potential (MEP) and electron density of the isolated molecules has been calculated with the Gaussian 09 facilities. The electron localization function

(ELF)⁵¹ has been obtained with the TOPMOD program.⁵² The molecules and the MEP and ELF isosurfaces have been represented with the Jmol program.⁵³

3. RESULTS AND DISCUSSION

We have computed all complexes that resulted from combining the acceptor and donor molecules included in Scheme 1 using a large variety of functionals and four ab initio methods, where the highest level CCSD(T)/aug-cc-pVTZ has been used as reference to analyze the reliability of the rest. We have divided this section into three parts, depending on the noncovalent interaction under study. In the fourth section, a general analysis of all the complexes studied in the present article has been carried out.

3.1. Halogen Bonding Complexes. The interaction energies and equilibrium distances of the halogen bonding complexes studied herein are gathered in Tables S1 and S2 of the Supporting Information. The statistical analyses of the interaction energies and intermolecular distances are shown in Tables 1 and 2.

Table 1. Statistical Analysis of the Energetic Results in the Halogen Bonded Complexes^a

method	R ²	slope	intercept	AAE	MAPE
M06-2X	0.997	1.02	0.82	2.3	2.1
RI-MP2	0.999	1.04	−5.76	10.2	10.8
MP2	0.996	1.05	−6.87	12.5	13.0
B3LYP	0.993	1.07	−6.38	13.9	14.3
PBE0	0.999	1.07	−10.77	17.8	19.2
APFD	0.999	1.05	−12.50	17.9	19.7
HSE06	0.999	1.07	−11.70	19.7	21.2
B97-D	0.984	1.08	−15.46	23.7	25.6
BLYP	0.966	1.15	−12.80	28.9	29.7
B97-D3	0.983	1.11	−18.33	29.7	31.8
BLYP-D3	0.968	1.09	−22.30	31.4	34.3
BP86	0.978	1.15	−18.89	34.6	36.6
BP86-D3	0.981	1.09	−27.48	37.1	41.0
HF	0.885	0.63	8.86	48.4	46.7

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

The halogen bond interactions have been rationalized in the literature^{5,6,10} as the interaction of a positive region of the molecular electrostatic potential in the halogen bond donor (FCl and FBr in this study) and an electron donor group. In Figure 1a, the MEP plots on the 0.001 au electron density isosurface of FCl and FBr have been represented. In both cases, a positive region of the MEP is found along the FX bond that corresponds to the σ -hole. The larger value of the positive MEP on the FBr molecule than in the FCl indicates that the former should be a better halogen bond donor than the former. The ELF isosurface (Figure 1b) of two representative complexes studied in this section are included. In both cases, the lone pair of ammonia points toward the σ -hole of the halogen bond donors.

From the results, interesting points arise. In the anionic complexes, all methods overestimate the interaction (apart from the HF method), especially the pure functionals where the overestimation is very large (up to 34 kJ/mol for BP86-D3!). As expected, the MP2 and RI-MP2 methods provide almost identical energies and distances. However, these ab initio

Table 2. Statistical Analysis of the Intermolecular Distance in the Halogen Bonded Complexes^a

method	R ²	slope	intercept	AAE	MAPE
M06-2X	0.993	0.99	0.01	0.012	0.5
B3LYP	0.961	1.14	−0.34	0.022	0.9
BP86-D3	0.903	1.22	−0.55	0.033	1.4
HSE06	0.959	1.15	−0.41	0.034	1.4
BP86	0.895	1.24	−0.60	0.034	1.5
APFD	0.959	1.14	−0.37	0.035	1.5
B97-D	0.937	1.23	−0.55	0.037	1.5
PBE0	0.957	1.15	−0.40	0.041	1.7
B97-D3	0.921	1.27	−0.65	0.041	1.7
RI-MP2	0.983	1.22	−0.58	0.043	1.8
BLYP	0.908	1.24	−0.55	0.049	2.0
BLYP-D3	0.915	1.22	−0.51	0.051	2.1
MP2	0.976	1.06	−0.20	0.055	2.3
HF	0.139	0.43	1.62	0.252	10.5

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

methods also overestimate the interaction (>11 kJ/mol), especially in the Br[−]:ClF complex. The best functional is M06-2X that gives results almost identical to those of the benchmark CCSD(T)/aug-cc-pVTZ level of theory and has even a better performance than the MP2 method and the rest of the hybrid functionals. PBE0, HSE06, and APFD functionals behave almost the same regarding both interaction energies and equilibrium distances. With respect to the neutral complexes, the differences between the methods are smaller because the energetic values are also smaller (in absolute value) compared to anionic complexes. However, in some cases, the overestimation of some pure functionals is considerable. For instance, the B97-D3 functional gives an interaction energy of −66.01 kJ/mol for the H₃N:ClF complex, whereas the reference is only −42.37 kJ/mol.

In general, the best method, in the cases studied, is the M06-2X with only an average deviation of 2.1% of the energy provided by the CCSD(T) method, followed by the RI-MP2 and MP2 ones. Large overestimations are observed in the interaction energies (between 25% and 41%) in the dispersion-corrected DFT methods, which advice against their use.

With respect to the equilibrium distances (see Table 2 and Table S2, Supporting Information), the differences with the CCSD(T) method are, in general, not very significant, with the exception of the HF method. In most cases (particularly pure functionals), they are shorter than the reference, in concordance with the overestimation of the interaction energy. The statistical analysis shows that the best results are obtained with the M06-2X method and the worse ones, excluding the HF method, correspond to the MP2 intermolecular distances with an average error of only a 2.3%. Thus, all the methods provide a reasonable geometrical description of the complexes considered.

3.2. Chalcogen Bonding Complexes. We have studied two types of chalcogen bonding complexes, depending on the number of σ -holes in the chalcogen atom that is determined by its hybridization (Figure 2a). The F₂S and F₂Se compounds present two σ -holes, each one due to the F–S/Se bond. In the rest of the compounds (F₂CS/Se and F₃PS/Se), a single σ -hole is observed along the CS/Se and PS/Se bonds. The ELF isosurface of some neutral (Figure 2b) and charged complexes

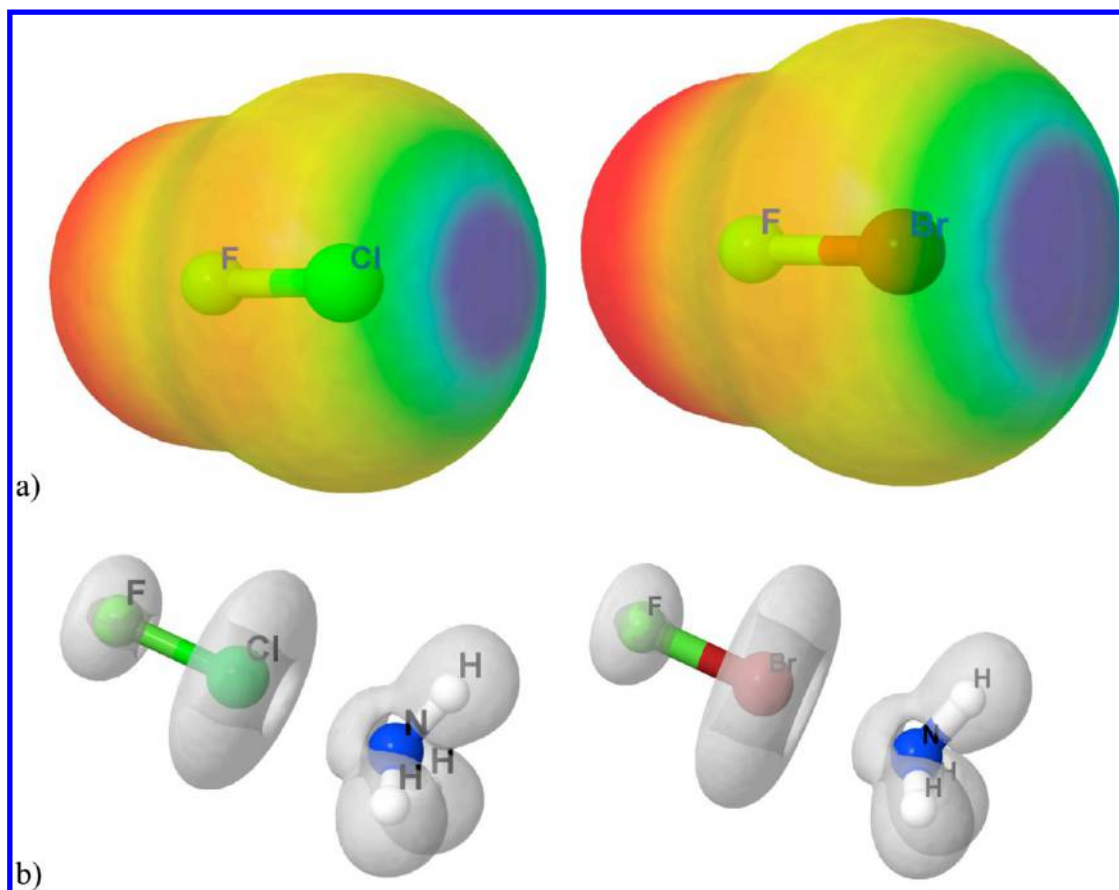


Figure 1. (a) MEP on the 0.001 au electron density isosurface of FCl and FBr. Color scheme spanning between -0.015 (red) to 0.05 (blue). (b) ELF at 0.75 isosurface of the two neutral complexes.

(Figure 2c) shows that the lone pairs of the ammonia points toward the location of the σ -hole of the chalcogen atoms, avoiding the regions where the lone pairs of the latter atoms are located, except in the F_2CS/Se complexes with anions probably due to the presence of a secondary interaction between the anions and the C atom.

In Tables S3 and S4 (Supporting Information), we summarize the results obtained using ChF_2 ($Ch = S, Se$) molecules as Lewis acids. The geometries obtained correspond to the “A” binding mode represented in Figure 3, where the $F-S\cdots D$ (donor atom) angle is close to 180° .

From the energetic results of Table 3 and Table S3 (Supporting Information), it is clear that the chalcogen bonding interaction with anionic donors is overestimated by all methods (either DFT or MP2). However, the overestimation is not as important as that previously found for the halogen bond (*vide infra*). The highest overestimation corresponds to the $Cl^-:SeF_2$ complex at the BP86-D3 level of theory that predicts a binding energy 20 kJ/mol higher than the reference level. The hybrid functionals B3LYP and M06-2X provide the best results. Regarding the neutral complexes, the general tendency is also to slightly overestimate the interaction energy, apart from BLYP and B3LYP functionals. In all cases (anionic and neutral complexes), the HF method gives very poor results with a strong underestimation of the interaction.

With respect to the equilibrium distances, all methods apart from HF give reasonable distances, in comparison to the CCSD(T) method. For the neutral complexes, the use of dispersion-corrected functionals is not recommended, since this

correction contributes to increment the overestimation. Finally, as previously noted for the halogen bonding interaction, PBE0, HSE06, and APFD functionals provide very similar binding energies and equilibrium distances.

As explained above, we have also analyzed chalcogen bonding complexes that are characterized by the sp^2 hybridization of the chalcogen atom. This type of complex has been scarcely studied in the literature. The features of these complexes are somewhat more similar to halogen bonding complexes since the chalcogen atom only has one σ -hole. However, the MEP value measured at this σ -hole is generally less positive than the value computed in any of both σ -holes of the related sp^3 -hybridized chalcogen. Obviously, this is due to the presence of the electronegative fluorine atoms directly bonded to the chalcogen atom in the F_2Ch molecule.

In Tables S5 and S6 (Supporting Information), we summarize the interaction energies and equilibrium distances computed for the complexes involving the $CF_2=Ch$ ($Ch = S, Se$) type molecules. These complexes present two different dispositions depending on the nature of the interacting molecule (neutral or charged), as shown in Figure 3. In the neutral complexes, the ammonia is located along the $C=Ch$ bond, whereas, in the charged complexes, a nonlinear $CF_2=Ch\cdots D$ disposition is observed in all the methods except from the HF one. The interaction energies are less favorable than those reported in Table S3 (Supporting Information) for the $F_2Ch\cdots D$ complexes, in agreement with the MEP results. Interestingly, the behavior of anionic and neutral complexes is the opposite. That is, the interaction energy of anionic

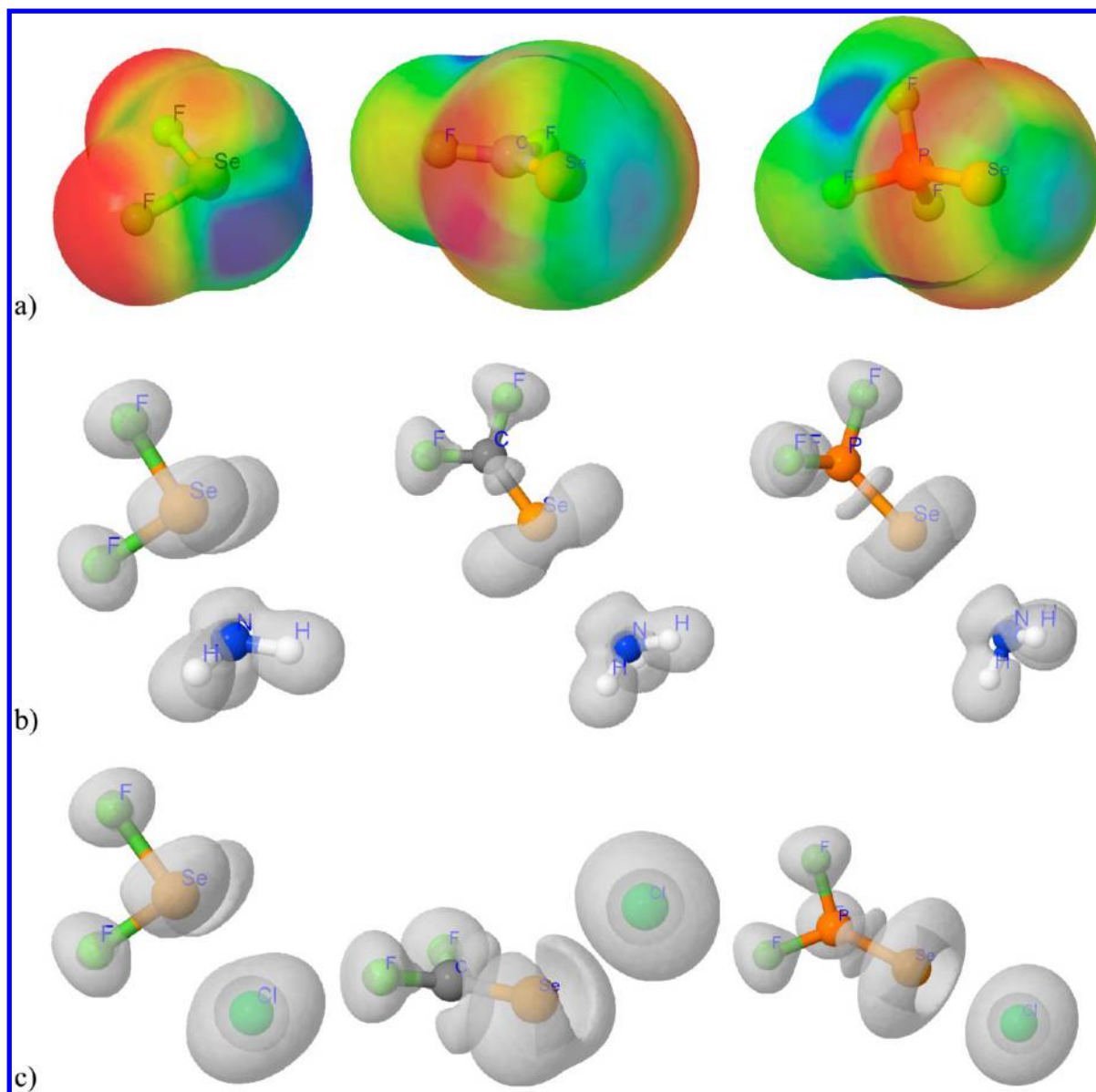


Figure 2. (a) MEP on the 0.001 au electron density isosurface of F_2Se , F_2CSe , and F_3PSe . Color scheme spanning between -0.015 (red) to 0.05 (blue). (b) ELF at 0.75 isosurface of three neutral complexes. (c) ELF at 0.75 isosurface of three charged complexes.

complexes is overestimated by the DFT and MP2 methods and it is underestimated in neutral complexes. Again, the functionals that give better results are the hybrid B3LYP and M06-2X methods. The underestimation observed in neutral complexes originates that, for this particular class of complexes, the inclusion of the correction for dispersion improves the agreement with the CCSD(T) results, and therefore, it is recommended. The nonlinear geometry of these complexes can be, in part, rationalized analyzing the MEPS depicted in Figure 2. An σ -hole in both $CF_2=S$ and $CF_2=Se$ molecules can be appreciated; however, there is not a negative belt around the chalcogen atom. Instead, a region of positive potential (green isosurface) is found that connects the σ -hole with the π -hole (over the carbon atom). Probably, another contribution to the interaction energy, apart from the electrostatic term, contributes to the geometry of these complexes, where the $F_2C=Ch\cdots D$ angle varies from 127° to 132° for the anionic complexes. Polarization effects likely contribute to this deviation from

linearity since the polarization of the π -system increases as the angle approximates to 90° .

Regarding the quality of the DFT results in anionic complexes, larger differences are observed for the BP86-D3 and B97-D3 functionals and, in general, the hybrid functionals are adequate for describing these complexes. As is also observed in previously described $F_2Ch\cdots D$ complexes, neutral complexes behave contrarily and the energies are underestimated by DFT methods, and consequently, the use of D3 correction is recommended. In addition, MP2 methods are better than DFT ones to describe both $F_2C=Ch\cdots D$ and $F_2Ch\cdots D$ neutral complexes.

Finally, we have also studied the chalcogen complexes using the $F_3P=Ch$ ($Ch = S, Se$) as acceptors. The main difference with the other sp^2 -based complexes is that the chalcogen atom has a genuine negative belt resembling a halogen atom (see Figure 2). Therefore, these complexes are characterized by adopting the "C" geometry depicted in Figure 3. In addition, the σ -hole is more pronounced in these molecules than in

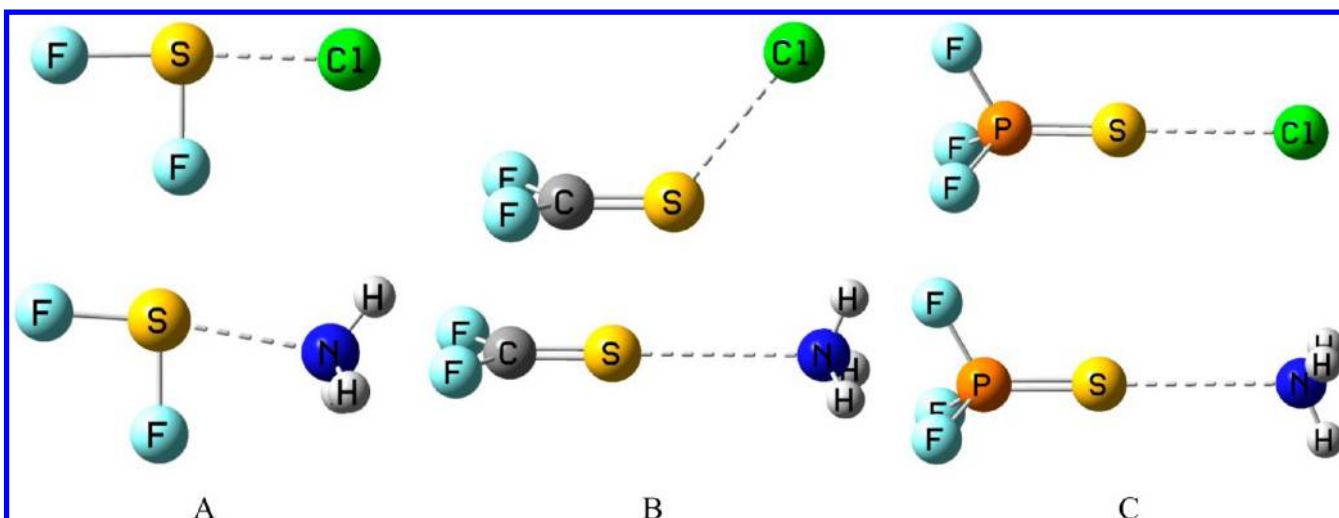


Figure 3. Optimized geometries of selected complexes considered in this section at the MP2/aug-cc-pVTZ computational level. The three different binding modes (A, B, and C) observed in chalcogen bonding complexes are indicated.

Table 3. Statistical Analysis of the Interaction Energies in the Chalcogen Bonded Complexes^a

method	R ²	slope	intercept	AAE	MAPE
RI-MP2	0.999	1.05	−0.89	3.3	7.8
M06-2X	0.997	1.08	1.62	3.2	8.3
MP2	0.997	1.07	−1.50	4.6	10.7
APFD	0.997	1.13	0.45	5.9	12.3
PBE0	0.998	1.15	2.93	5.2	14.2
B3LYP	0.997	1.09	3.71	3.2	14.6
HSE06	0.998	1.15	1.58	6.5	16.3
B97-D	0.990	1.09	−1.72	6.6	17.0
B97-D3	0.985	1.13	−4.35	10.8	25.0
BLYP-D3	0.973	1.13	−6.10	12.1	29.2
BLYP	0.965	1.15	−1.33	10.5	31.3
BP86-D3	0.976	1.18	−6.55	15.1	35.1
BP86	0.970	1.21	−1.81	13.4	36.7
HF	0.951	0.67	10.04	25.3	65.6

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

Table 4. Statistical Analysis of the Intermolecular Distance in the Chalcogen Bonded Complexes^a

method	R ²	slope	intercept	AAE	MAPE
RI-MP2	0.998	1.01	−0.07	0.038	1.3
M06-2X	0.892	0.90	0.30	0.046	1.7
MP2	0.993	1.00	−0.06	0.049	1.7
APFD	0.879	0.94	0.15	0.076	2.8
B3LYP	0.851	0.89	0.34	0.085	3.0
B97-D	0.834	0.86	0.43	0.090	3.3
HSE06	0.887	0.92	0.18	0.095	3.4
PBE0	0.885	0.97	0.06	0.098	3.5
B97-D3	0.782	0.73	0.72	0.109	3.7
BLYP-D3	0.786	0.71	0.81	0.108	3.9
BLYP	0.758	0.79	0.61	0.121	4.2
BP86	0.781	0.75	0.65	0.134	4.6
BP86-D3	0.800	0.69	0.80	0.142	4.8
HF	0.574	0.92	0.69	0.481	16.8

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

F₂C=Ch ones. Therefore, the F₃P=Ch...D angle is close to 180° at all levels of theory.

The energetic and geometric results obtained for the F₃P=Ch...D complexes are gathered in Tables S7 and S8 (Supporting Information), respectively. Regarding the reliability of the functionals, the interaction energies for complexes involving anions are overestimated by the pure functionals (especially PB86-D3) and are well-described by the hybrid functionals. The energies are underestimated in neutral complexes, apart from the dispersion-corrected functionals. In this case, the B97-D3 and APFD give good results in conjunction with the MP2 methods.

The statistical comparisons of the energetics and geometric results of all the chalcogen bonded complexes (18 cases) with the different computational methods are gathered in Tables 3 and 4, respectively. From the statistical analysis, the RI-MP2 is the best computational method, closely followed by the M06-2X and MP2 methods. As in the case of the halogen bonds, the inclusion of empirical dispersion corrections provides large errors.

Regarding the best geometrical description of the complexes (Table 4), the results parallel those obtained for the energy, being the first three methods: RI-MP2, M06-2X, and MP2. In these complexes, the average errors observed in the DFT methods can be up to 4.8% compared to the CCSD(T) ones.

3.3. Pnictogen Bonding Complexes. The interaction energies and equilibrium distances obtained for pnictogen bonding complexes are summarized in Tables S9 and S10 (Supporting Information), respectively. The MEPs of the isolated pnictogen donors (PF₃ and AsF₃) are gathered in Figure 4a, and the ELF isosurface of selected complexes is shown in Figure 4b. As in previous cases, positive MEP values are obtained along the FX bonds and, within the complexes, this region points toward the location of the lone pair electrons of ammonia (Figure 4b).

From the inspection of the energetic results, it is clear that the differences in interaction energies observed for the anionic complexes are small, in contraposition to the results observed for halogen and sp³-chalcogen complexes (see Tables S1 and S3, Supporting Information). Only the HF method gives

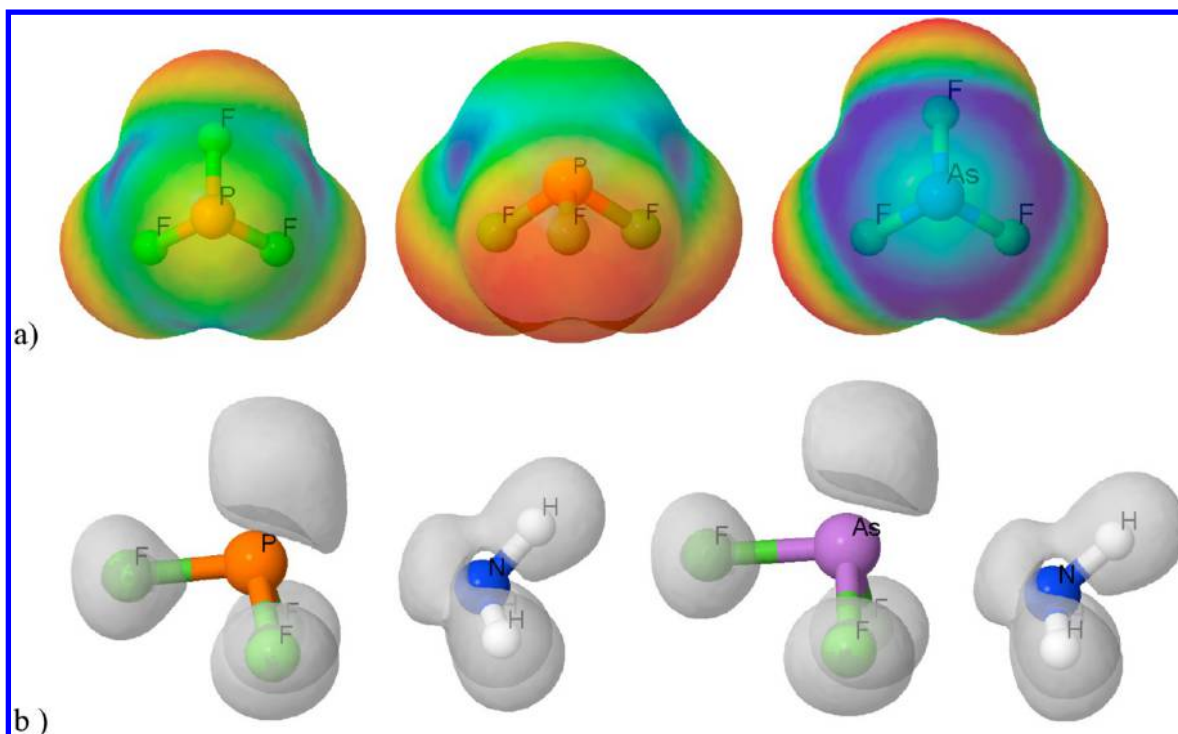


Figure 4. (a) MEP on the 0.001 au electron density isosurface of F₃P (two views) and F₃As. Color scheme spanning between -0.015 (red) to 0.05 (blue). (b) ELF at 0.75 isosurface of the two neutral complexes.

unreliable results. For the neutral complexes, the pure functionals without correction for dispersion underestimate the interaction and the rest of the functional provides acceptable results.

The statistical analysis of the results (Tables 5 and 6) indicates that the method with the smaller MAPE is the RI-

Table 5. Statistical Analysis of the Interaction Energies in the Pnicogen Bonded Complexes^a

N = 6	R ²	slope	intercept	AAE	MAPE
RI-MP2	0.999	1.02	-0.60	2.2	4.0
B97-D	0.997	1.02	1.94	2.0	4.7
MP2	0.995	1.04	-1.18	3.8	6.4
BLYP-D3	0.995	1.07	1.40	4.0	6.4
B97-D3	0.995	1.07	1.18	4.1	6.5
HSE06	0.997	1.10	2.49	4.9	7.5
PBE0	0.997	1.10	3.25	4.5	7.7
APFD	0.998	1.07	-1.44	5.9	9.5
B3LYP	0.998	1.06	7.71	3.9	11.1
BP86-D3	0.992	1.11	-0.86	7.6	11.1
BLYP	0.992	1.12	10.23	3.8	12.7
M06-2X	0.997	1.05	-4.71	7.6	13.8
BP86	0.988	1.16	7.78	6.6	14.6
HF	0.988	0.70	6.12	25.3	42.2

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

MP2, whereas the one with the smallest AAE is the B97-D one. However, the statistical of the linear regression are better for the RI-MP2 than the AAE ones (larger R² value and smaller slope). In these complexes, the M06-2X that was the best functional for the other two interactions (halogen and

Table 6. Statistical Analysis of the Intermolecular Distance in the Pnicogen Bonded Complexes^a

method	R ²	slope	intercept	AAE	MAPE
RI-MP2	0.990	1.01	-0.06	0.030	1.1
B97-D3	0.989	0.82	0.51	0.031	1.1
BLYP-D3	0.986	0.84	0.48	0.032	1.2
B3LYP	0.974	0.94	0.18	0.033	1.2
M06-2X	0.974	0.89	0.27	0.037	1.3
MP2	0.973	0.93	0.14	0.040	1.4
BP86	0.953	0.78	0.57	0.051	1.8
BLYP	0.937	0.90	0.33	0.050	1.8
B97-D	0.963	0.97	0.13	0.050	1.8
HSE06	0.977	0.84	0.39	0.056	2.0
BP86-D3	0.919	0.73	0.68	0.060	2.1
PBE0	0.975	0.84	0.38	0.063	2.2
APFD	0.943	0.85	0.35	0.067	2.4
HF	0.667	1.17	-0.12	0.368	13.3

^aThe values obtained at the CCSD(T)/aug-cc-pVTZ computational level are used as reference. The data are ranked based on the MAPE values.

chalcogen bonding) provides some of the largest average errors of all the DFT methods (13.8%).

The average absolute errors in the intermolecular distances are in a small range, between 0.030 and 0.067 Å, which corresponds to 1.1–2.4% of the calculated CCSD(T) distances. The RI-MP2 method provides distances more similar to those from the CCSD(T) one.

3.4. General Analysis of All the Complexes. We must note that the three sets are not equally populated. Of the 30 complexes, there are 6 halogen bonded (XB) complexes, 18 chalcogen bonded (ChB) complexes, and 6 pnicogen bonded (ZB) complexes, and this unbalanced situation will have consequences on the statistical analysis. A comparison of

methods from the best, that is, the closer to CCSD(T), to the worst for energies and geometries (Tables 7 and 8), excluding

Table 7. Ranking of the Different Methods Based on the MAPE Analysis of the Interaction Energy^a

ranking	All	XB	ChB	ZB
1	RI-MP2	M06-2X	RI-MP2	RI-MP2
2	M06-2X	RI-MP2	M06-2X	<i>B97-D</i>
3	MP2	MP2	MP2	MP2
4	APFD	B3LYP	APFD	<i>BLYP-D3</i>
5	B3LYP	PBE0	PBE0	<i>B97-D3</i>
6	PBE0	APFD	B3LYP	B3LYP
7	HSE06	HSE06	HSE06	PBE0
8	<i>B97-D</i>	<i>B97-D</i>	<i>B97-D</i>	APFD
9	<i>B97-D3</i>	<i>BLYP</i>	<i>B97-D3</i>	<i>BP86-D3</i>
10	<i>BLYP-D3</i>	<i>B97-D3</i>	<i>BLYP-D3</i>	B3LYP
11	<i>BLYP</i>	<i>BLYP-D3</i>	<i>BLYP</i>	<i>BLYP</i>
12	<i>BP86-D3</i>	<i>BP86</i>	<i>BP86-D3</i>	M06-2X
13	<i>BP86</i>	<i>BP86-D3</i>	<i>BP86</i>	<i>BP86</i>
number of complexes	30	6	18	6

^aThe seven best methods for the “All” set are in bold.

Table 8. Ranking of the Different Methods Based on the MAPE Analysis of the Intermolecular Distances^a

ranking	All	XB	ChB	ZB
1	RI-MP2	M06-2X	RI-MP2	RI-MP2
2	M06-2X	B3LYP	M06-2X	<i>B97-D3</i>
3	MP2	<i>BP86-D3</i>	MP2	<i>BLYP-D3</i>
4	B3LYP	HSE06	APFD	B3LYP
5	APFD	<i>BP86</i>	B3LYP	M06-2X
6	B97-D	APFD	B97-D	MP2
7	HSE06	B97-D	HSE06	<i>BP86</i>
8	<i>B97-D3</i>	<i>PBE0</i>	<i>PBE0</i>	<i>BLYP</i>
9	<i>PBE0</i>	<i>B97-D3</i>	<i>B97-D3</i>	B97-D
10	<i>BLYP-D3</i>	RI-MP2	<i>BLYP-D3</i>	HSE06
11	<i>BLYP</i>	<i>BLYP</i>	<i>BLYP</i>	<i>BP86-D3</i>
12	<i>BP86</i>	<i>BLYP-D3</i>	<i>BP86</i>	<i>PBE0</i>
13	<i>BP86-D3</i>	MP2	<i>BP86-D3</i>	APFD
Number of complexes	30	6	18	6

^aThe seven best methods for the “All” set are in bold.

the HF methods that provide, in all cases, very poor results. We have separated the results of the analysis of all complexes in two blocks, the seven best results (bold) and the six worst results (italic).

Table 7 shows that XB and ChB behave like the “All” set, the two best methods being always RI-MP2 and M06-2X, followed by MP2; the remaining DFT methods only show that HSE06 is the worst. In the lower part of Table 7, BP86 and BP86-D3 appear to be the worst methods. Unfortunately, the weaker pnictogen bonds behave more erratically; although the two ab initio methods, RI-MP2 and MP2, are among the best ones, the DFT ones are unrelated to those of other bonds. B3LYP and PBE0 are in the top part of Table 7, but unsatisfactory methods, such as B97-D, BLYPD3, and B97-D3, perform rather well, whereas methods like APFD, B3LYP, and mainly M06-2X yield bad results.

The situation regarding geometries (Table 8) is similar, but owing to the fact that the variations in geometry are much smaller than the variations in energy, the homogeneity is not as good. Even so, the “All” and the ChB sets are almost identical

(but remember that 18 of the 30 values of the “All” set came from ChB data). One of the most unexpected results is the fact that, for halogen bonds, both ab initio methods, RI-MP2 and MP2, do not perform well. To have good geometries of the three individual sets, the best compromises are the RI-MP2 ab initio method and M06-2X and B3LYP DFT methods.

4. CONCLUDING REMARKS

From the results reported in this article, the following conclusions can be extracted:

1. Apart from the M06-2X method, all other DFT and MP2 ab initio methods largely overestimate the halogen bonding interaction when the donor is anionic (Cl^- and Br^-). The same result is also observed in neutral complexes. The use of dispersion-corrected methods is not recommended to properly describe this interaction.
2. The chalcogen bonding interaction is more favorable in sp^3 than in sp^2 -hybridized chalcogen atoms. Regarding the reliability of the functionals, the hybrid B3LYP and M06-2X give good results for both anionic and neutral complexes, whereas the rest overestimate the interaction in $\text{F}_2\text{Ch}\cdots\text{D}$ complexes.
3. In chalcogen bonding complexes involving sp^2 -hybridized chalcogen atoms, an overestimation of the anionic complexes and an underestimation of the neutral complexes are observed for most functionals. The hybrid B3LYP and M06-2X give good results for anionic complexes, and the use of dispersion-corrected functionals is recommended for neutral complexes. The MP2 method gives very good results in all neutral chalcogen bonding complexes.
4. The pnictogen bonding complexes are well-described by most functionals apart from the M06-2X and BP86-D3 methods.

■ ASSOCIATED CONTENT

Supporting Information

Interaction energies and equilibrium distances of all complexes studied herein at all levels of theory (Tables S1–S10), BSSE results (tables of energies, distances, and statistical analysis, Tables S11–S19), and Cartesian coordinates of CCSD(T)/aug-cc-pVTZ optimized complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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