

Accepted Manuscript

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PII: S1093-3263(15)00029-7
DOI: <http://dx.doi.org/doi:10.1016/j.jmgm.2015.01.010>
Reference: JMG 6511

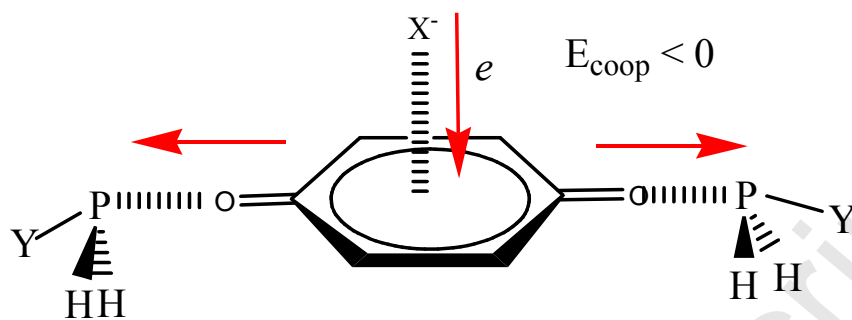
To appear in: *Journal of Molecular Graphics and Modelling*

Received date: 13-11-2014
Revised date: 26-12-2014
Accepted date: 26-1-2015

Please cite this article as: M.D. Esrafilifar^F, Mohammadian-Sabet, M. Solimannejad, Mutual influence between anion- π and pnictogen bond interactions: The enhancement of $P\cdots N$ and $P\cdots O$ interactions by an anion- π bond, *Journal of Molecular Graphics and Modelling* (2015), <http://dx.doi.org/10.1016/j.jmgm.2015.01.010>

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Graphical abstract.



Research Highlights:

- 1) The interplay between anion- π and pnictogen bond interactions is studied.
- 2) The cooperative energy ranges from -1.8 to -4.1 kcal mol⁻¹.
- 3) The complexes in which weaker Pn-bond is present exhibit strong cooperativity.
- 4) When the anion is F⁻, shortening of P \cdots N/O appears more pronounced.

Mutual influence between anion- π and pnictogen bond interactions: The enhancement of $P\cdots N$ and $P\cdots O$ interactions by an anion- π bond

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Abstract

In this work, the interplay between anion- π and pnictogen bond interactions is investigated by ab initio calculations. Cooperative effects are observed in the studied complexes in which anion- π and pnictogen bond interactions coexist. These effects are analyzed in detail in terms of the energetic, geometric, charge-transfer and electron density properties of the complexes. The cooperative energy ranges from -1.8 to -4.1 kcal mol⁻¹. The effect of an anion- π bond on a pnictogen bond is more pronounced than that of a pnictogen bond on an anion- π bond. The enhancing mechanism is analyzed in views with the charge-transfer, electrostatic potential and electron density analysis.

Key words: anion- π ; pnictogen bond; interplay; ab initio; QTAIM.

1. Introduction

Noncovalent interactions are of great importance in many physical, chemical, and biological systems. They are very important for the structures and stabilities of a broad range of molecular complexes and crystals [1,2]. Among them, hydrogen-bonding is the most widely studied one and has been extensively studied from both theoretical and experimental viewpoints [3,4]. While hydrogen-bonding has been acknowledged for a long time, however, considerable attention has been paid recently to other intermolecular interactions. Currently, halogen-bonding [5-15] is becoming one of the most intensively investigated of such interactions, due to its extensive potential applications in molecular recognition, drug design and crystal engineering. It is an interaction between a halogen atom (X) in one molecule and an atom with an excess of electron charge density in another molecule. A halogen bond can be described in general by $RX \cdots YZ$ interaction, in which RX is usually an organic halide (almost always a chloride, bromide, or iodide), and YZ is a Lewis base, Y is a negative site, most often an atom such as F, O, and N with lone-pair electrons. Since in the halogen bond, the electron acceptor is often a negatively charged halogen atom, the attractive interaction between X and Y atoms may appear to be counterintuitive. A reasonable explanation for this puzzling phenomenon came from Auffinger et al. [16], Politzer et al. [17], and Clark et al. [18] who showed the existence of an electropositive crown (the region of diminished electron density) at the top of the halogen atom directed toward the electron donor. This positive potential on the halogen is usually labeled as “ σ -holes”. If the depletion is sufficient, the σ -hole acquires a positive electrostatic potential, i.e. a positive σ -hole, which can interact with a negative site. Although not as thoroughly investigated as either hydrogen or halogen bonds, there have been a number of reports that pnictogen atoms can serve a similar function in what might analogously be referred a “pnictogen bond”.

The pnictogen bond is a Lewis acid–Lewis base attractive interaction in which a pnictogen atom (N, P, As or Sb) act as the Lewis acid [19-22]. Politzer and Murray [23,24] associated its origin with the presence of an σ -hole in the prolongation of the R–Pn bond (where R is an electron-withdrawing group and Pn is a pnictogen atom), that interacts with an electron-rich moiety of a Lewis base (B) through an essentially electrostatic $R-Pn \cdots B$ interaction. The size of the σ -hole increases with pnictogen size in going from the lighter to the heavier atoms, as polarizability increases and electronegativity decreases. Thus, the electrostatic component of the

Pn-bond has been described in terms of the σ -hole concept. However, Scheiner [25,26] and Alkorta et al. [27–29] have demonstrated that charge-transfer from the lone pair of the Lewis base to the $\sigma^*_{\text{Pn-R}}$ orbital of the acid plays an essential role in the stabilization of Pn-bond complexes. Pn-bond interactions are relevant in biological systems. For instance, the $\text{P}\cdots\text{N}$ interactions were found in protein β -sheets [30]. The Pn-bonds involving Sb atom also likely participate in the mechanism of inhibition of Sb-based drugs used to treat leishmaniasis [31].

The cooperativity is one of the interesting characteristics of intermolecular interactions [32]. Like hydrogen bonds, the Pn-bond exhibits cooperative effects with itself [33] or other types of interactions [34,35]. Such effect can enhance Pn-bond strength and makes the complex systems more stable. Recently, an extensive study on the cooperativity of Pn-bond in linear $(\text{PH}_2\text{F})_{2-7}$ and $(\text{PH}_2\text{Cl})_{2-7}$ complexes has been reported by our group [33]. The interaction energy of $\text{P}\cdots\text{F}$ interaction increases from $-9.66 \text{ kcal mol}^{-1}$ in $(\text{PH}_2\text{F})_2$ to $-12.20 \text{ kcal mol}^{-1}$ in $(\text{PH}_2\text{F})_7$ cluster. The cooperative effects between Pn-bond and halogen bond interactions were studied by Li and coworkers [34] for $\text{XCl}\cdots\text{FH}_2\text{P}\cdots\text{NH}_3$ ($\text{X}=\text{F}, \text{OH}, \text{CN}, \text{NC}, \text{ and FCC}$) complexes. Interestingly, the increased percentage is more prominent for the interaction energy of the halogen bond.

The interactions involving aromatic rings are very important in many fields. For instance, π - π stacking [36], cation- π , [37] anion- π [38] and $\text{CH}-\pi$ [39] interactions have a critical role in many important chemical and biological processes including molecular recognition, crystal engineering and enzymatic mechanisms. In recent years, many studies on the properties and structures of anion- π bonds have been performed. In particular, Estarellas et al. [40] revealed cooperativity effects when anion- π and halogen bond interactions coexist in the same complex. Given the observation that the Pn-bond has some different features from the halogen bond, the question arises as to whether a different cooperative effect can be found when anion- π and Pn-bond interactions coexist in the same complex.

Herein we report a theoretical study to examine the mutual influence between anion- π and Pn-bond interactions. We selected four π -acidic heteroaromatic rings (**1–4**), shown in Figure 1, that contain substituent groups in the structure which can act as Pn-bond acceptors. Figure 2 indicates the schematic representation of isolated anion- π , Pn-bond and anion- π -Pn complexes studied here. To unveil the mechanism of the cooperativity effects, natural bond orbital (NBO)

and quantum theory of atoms in molecules (QTAIM) analyses are performed. The molecular electrostatic potential analysis is also applied here to deepen the origin of the cooperative effects.

2. Computational details

The geometries of all studied monomers and complexes were fully optimized at the MP2(full)/6-311++G** level of theory by using the GAMESS suite of programs [41]. Harmonic frequency calculations performed at the same level indicated that all the structures obtained correspond to energetic minima. Optimization of complexes **21–36** was carried out with imposition of C_{2v} symmetry. The interaction energies were estimated at the MP2(full)/6-311++G** level with corrections for the basis set superposition error (BSSE) by the counterpoise method of Boys and Bernardi [42]. The interaction energies in the complexes were obtained as the electronic energy difference between the complex and sum of the isolated monomers. Molecular electrostatic potentials were calculated with Wave Function Analysis–Surface Analysis Suite (WFA–SAS) developed by Politzer and coworkers [43]. NBO analysis [44] was performed by using the MP2 density at the MP2/6-311++G** level of theory. The topological analysis of the electron charge density was performed by means of the AIM2000 program [45] with the MP2/6-311++G** wave function.

3. Results and discussion

3.1. Energetic and geometric features of isolated anion- π and Pn-bond complexes. Table S1 lists the interaction energies and equilibrium distances of isolated anion- π **5–12** and Pn-bond **13–20** complexes at the MP2/6-311++G** level of theory. Some interesting points can be extracted from the interaction energy results. The interaction energies of anion- π complexes **5–12** are predicted to lie in the range from -9.3 to -32.6 kcal mol⁻¹, which compare favorably with the results of previous calculations [46–48]. The interaction energies of Pn-bond complexes are modest, in the range from -2.0 to -3.8 kcal mol⁻¹ for each Pn-bond interaction, because the aromatic rings are not electron-donating enough. As the electron-donating ability of the N or O atoms in compounds **1–4** decreases, the Pn-bond interaction energies become weaker (less negative), which has been demonstrated as well in earlier studies [23,24]. Thus, the hydrogenated rings form stronger Pn-bond compared to the fluorinated ones. This also agrees well with the finding that compounds **2** and **4** display less negative electrostatic potential on the nitrogen or oxygen atom (see Figure 1). The fact that compound **1** forms a stronger Pn-bond than that of **3** reveals that the C \equiv N group is a better electron donor than the C=O. This may be

attributed to the high basicity of the *sp*-hybridized nitrogen atom. Besides, PH₂F as Pn-bond donor forms stronger complexes than PH₂Cl in agreement with their σ -hole potential values (45.8 vs. 40.8 kcal mol⁻¹).

The optimized equilibrium anion- π distances in complexes **5–12** are in the range of 2.08–3.20 Å (Table S1). For a given ring, the anion- π distance becomes shorter when the polarizing power of anion increases (Cl⁻ < F⁻). Due the strong electron-withdrawing ability of the F substituents on the π systems, anion- π binding distances in the fluorinated complexes (**7,8** and **11,12**) appear somewhat shorter compared to the hydrogenated ones. The optimized equilibrium N \cdots P–Y and O \cdots P–Y contacts in complexes **13–20** are essentially linear; all of the predicted Pn-bond distances are considerably shorter than the sums of the van der Waals radii of the atoms involved [49], which further supports the presence of the Pn-bond interaction in these complexes. The linear Pn-bond structures can be understood with the electrostatic potentials of PH₂F and PH₂Cl molecules. As shown in Figure 1, these molecules have a region of positive electrostatic potential (σ -hole) along the extension of the covalent P–F and P–Cl bonds. These σ -holes represent attractive channels for the approach of a nucleophile to the PH₂F and PH₂Cl molecules. For **1–4**, the lone-pair electrons region outside the nitrogen or oxygen atom have an obvious negative electrostatic potential. The most negative values associated with the nitrogen or oxygen atoms are observed to be at points that would correspond to a linear Pn-bond interaction. Table S1 shows that Pn-bond distances in the ternary complexes **13–20** are predicted to lie in the range 2.81–2.87 Å and 2.86–2.97 Å for P \cdots N and P \cdots O, respectively. For a given Y, the compounds containing nitrogen atoms (**13–16**) form shorter Pn-bond distances than the oxygen-containing compounds (**17–20**), which reveals that nitrogen atom is a better Pn-bond acceptor than oxygen.

The presence of the ring critical points (RCP) of electron densities in the binary complexes **5–12** provides more evidence for the formation of the anion- π interaction. It has been proposed in numerous studies that the topological parameters of the RCP, such as electron density ρ , are very helpful for characterizing and quantifying anion- π or cation- π interactions [50,51]. Table S1 shows that the value of electron density at the RCP of anion- π complexes ranges from 0.015 to 0.020 au. Clearly, the electron density at these RCPs is not consistent with the E_{int} of anion- π interactions (Figure S1). The value of ρ at the P \cdots N/O bond critical point (BCP) is within a range from 0.008 to 0.014 au, which does fall within the proposed range of 0.002–0.035 au for hydrogen bonds [52]. This shows that the Pn-bond interactions also belong to

closed-shell interactions and the nature of $P\cdots N$ and $P\cdots O$ σ -hole interactions is no different than that hydrogen bonding. Figure S2 indicates that there is a linear relationship between the ρ_{BCP} value and the strength of the Pn-bond interactions in the Pn-bond complexes ($R^2=0.95$).

NBO theory can also provide some information on the formation and characteristics of the isolated anion- π and Pn-bond complexes. Table S1 indicates that on formation of binary systems **5–12**, a small net charge, in the range of 0.003–0.070 e, transfers from anion X^- to the aromatic molecules **1–4**, which act as Lewis acids. In contrast, in complexes **13–20**, charge-transfer (CT) from the aromatic molecule, which functions as Lewis bases, to PH_2Y molecules occurs. The largest CT happens in the complex **13**, whereas the smallest CT is seen in the complex **20**. In fact, for the isolated Pn-bond complexes under study, an acceptable correlation is found between CT values and interaction energies (Figure S3). This means that the orbital interaction plays an important role in the Pn-bond interaction.

3.2. Cooperativity in multicomponent anion- π and Pn-bond complexes

The energetic and geometric results computed for multicomponent complexes **21–36** are summarized in Table 1. The total interaction energies of multicomponent complexes range from -22.9 to -47.3 kcal mol⁻¹. One can see that the interaction energy in the F^- complexes is more negative than the Cl^- counterpart. As the electron-accepting ability of the ring in compounds **1–4** increases, the E_{int} become stronger (more negative). Hence, the fluorinated rings form stronger complexes compared to the hydrogenated ones.

Table 1 also summarizes the evaluated cooperativity energy E_{coop} in the multicomponent systems. This term is intended to provide an estimation of the “extra” energetic stabilization obtained in multicomponent complexes as a result of the interplay of both interactions. It is computed with formulas of

$$E_{coop}=E_{int}(anion-\pi-Pn)-E_{int}(anion-\pi)-E_{int}(Pn-bond)-E_{int}(Pn-PH_2Y) \quad (1)$$

where $E_{int}(anion-\pi)$, $E_{int}(Pn-bond)$ and $E_{int}(anion-\pi-Pn)$ are the interaction energies of the corresponding optimized anion- π , Pn-bond and anion- π -Pn complexes, respectively. $E_{int}(Pn-PH_2Y)$ is the interaction of the anion- PH_2Y units in the anion- π -Pn complexes. The calculated E_{coop} are listed in the third column of Table 1. In all anion- π -Pn complexes **21–36** studied, a favorable cooperativity is found with values that range between -1.8 and -4.1 kcal mol⁻¹. These negative E_{coop} values indicate that a positive cooperative effect is present between the anion- π and Pn-bond interactions. That is, the mutual influence of the two interactions is transmitted

through the π -bonds from the anion X^- to the PH_2Y molecule and vice versa. With increasing the interaction energy of anion- π , the cooperative energy between them also grows. From Table 1 results, one can see that the computed E_{coop} values are modest for complexes **35** and **36** because the Pn-bond interaction is weak. Nevertheless, cooperative effects between the two interactions contribute 5.5% of the total interaction energy of the anion- π -Pn complexes. For the rest of complexes, the E_{coop} values are significant, especially in complex **29** and **30**, that is, the C=O group becomes strong electron donor as a consequence of participation of the aromatic ring in anion- π interactions. On the other hand, for a given X^- and π -system, the complexes in which weaker Pn-bond donor SHCl is present exhibit strong cooperativity, while weak cooperativity occurs in the complexes involving SHF. That is, the weaker Pn-bond interaction shows a larger increased percentage of the interaction energy due to another stronger interaction, which has been well documented in previous studies of the interplay between two different types of interactions [33,34].

Table 1 presents the binding distances of the anion- π and Pn-bond interactions in the multicomponent complexes. It is clear that for the complexes **21–36**, the anion- π bond distances are shorter than those in the corresponding isolated **5–12** complexes, that is, the presence of the pnictogen bond interaction strengthens the anion- π interaction. We noted, however, the shortening of each anion- π bond distance in the complexes **21–36** is dependent on the strength of the $P\cdots N/O$ bond and it becomes larger with an increase in the Pn-bond strength. A same behavior is also observed for the $P\cdots N/O$ bond distances. The polarization of the rings **1–4** by the X^- anion makes the nitrogen or oxygen atom more negative, thereby increasing the attraction within the $P\cdots N/O$ interaction. When the anion is F^- , shortening of $P\cdots N/O$ appears more pronounced, that is, the addition of strong anion- π interaction strengthens Pn-bond interaction to a greater degree. The shortening of the $P\cdots N/O$ distances in the complexes **21–36** are dependent on the strength of the Pn-bond interaction and it becomes larger for the weaker Pn-bond interactions. This means that the mutual influence of the two interactions depends on the Pn-bond strength. Figure 3 shows the relationship between the cooperative energies E_{coop} and corresponding $\Delta R_{Pn-bond}$ values. The linear correlation coefficient is 0.96. This reveals that the cooperative effects may play a role in the formation and stability of the anion- π -Pn complexes.

The different energetic and geometric effects evident in the multicomponent complexes under investigation can be rationalized by the molecular electrostatic potential analysis. The

most positive ($V_{S,max}$) and most negative ($V_{S,min}$) electrostatic potentials of the monomers **1–4** and anion- π systems **5–12** are listed in Table 2. There is a negative electrostatic potential of -33.4 and -26.6 kcal mol⁻¹ on the nitrogen surface of **1** and **2** molecules, respectively. One can see that the X^- anion has the ability to enhance the size of the $V_{S,min}$ upon the formation of anion- π interaction. For example, it is -92.0 and -87.9 kcal mol⁻¹ for the complexes **5** and **6**, respectively. This means that the nitrogen atom in the mentioned complexes is a better electron donor than that of molecule **1**. Upon anion- π bond formation, the $V_{S,min}$ value associated with the oxygen atoms of **3** and **4** becomes also more negative. It is seen from Table 2 that the negative electrostatic potentials of nitrogen or oxygen atoms of F^- - π are much larger than those of Cl^- - π ; this can presumably be attributed to greater polarizing power of the former anion. Besides, the hydrogenated rings have larger $V_{S,min}$ values compared to fluorinated ones. This means that the nitrogen or oxygen atom in the hydrogenated systems **5**, **6**, **9** and **10** is a better electron donor. Thus, the electron density flows from anion X^- to the ring, causing a more negative $V_{S,min}$ on the nitrogen or oxygen atom.

The variation in the electron density ρ value at the RCPs or BCPs of the multicomponent systems with respect to the isolated anion- π and Pn-bond complexes can be used to analyze the mutual influence of the two interactions. The results are listed in Table 3. The values of electron density at the RCPs, ρ_{RCP} , are in the range of 0.016–0.022 au in the complexes **21–36**. Table 3 results reveal that the ρ_{RCP} values in the all anion- π -Pn complexes are slightly larger than those in the isolated complexes **5–12**. These results confirm that the anion- π interaction in the complexes **21–36** is reinforced with respect to the isolated systems. When the anion is F^- , greater values of $\Delta\rho_{RCP}$ are predicted, in good agreement with strong cooperativity found in the complexes involving F^- . A same behavior is observed for the values of ρ_{BCP} at the $P\cdots N/O$ critical points that characterizes the Pn-bond interaction. The increase of the ρ_{BCP} value at the $P\cdots N/O$ critical points is the largest in the complexes **29** and **30**, which shows a strong cooperativity as noted above. For a given complex, the computed value of $\Delta\rho_{BCP}$ is larger than the corresponding $\Delta\rho_{RCP}$ value, and this is further confirmation that the presence of anion- π influences Pn-bond interactions greatly. These results are in agreement with the binding distances changes ΔR in Table 1, indicating that the effect of anion- π on the properties of Pn-bond is significant than that of Pn-bond on the properties of anion- π .

To estimate the contribution to the cooperativity of anion- π and Pn-bond interactions from orbital interactions, the CT values in the multicomponent complexes were computed. These CTs are listed in Table 3, and a clear correlation with the other properties is evident. That is, the stronger the anion- π and Pn-bond interaction, the larger is the magnitude of the CT. It is clear that for the complexes **29–36**, the CT in the anion- π interaction is larger than that in the Pn-bond. However, the difference of the $CT_{\text{anion-}\pi}$ between the anion- π -Pn and isolated anion- π is small. This reveals that the orbital interaction is of little importance for the enhancement of the anion- π in the anion- π -Pn complexes. The calculated CT values in the anion- π bonds of the anion- π -Pn systems are slightly greater than those in the binary anion- π complexes **5–12**, which implies strengthening of anion- π bonds. A same behavior is also evident for the $CT_{\text{Pn-bond}}$ values of Pn-bond interactions. The results are consistent with the optimized binding distance and interaction energy values. A possible explanation for this finding might be that when a small quantity of charge is transferred between the anion X^- and ring (i.e. $X^- \rightarrow \pi$ interaction), the aromatic ring acquires slight anionic character. This lowers the energy of its filled orbitals and renders them more spatially diffuse. Thus, the nitrogen or oxygen atoms of binary complexes **5–12**, inherently become an improved donor for concerted anion- π -Pn interaction.

4. Conclusion

Ab initio calculations were performed to study the interplay between anion- π and Pn-bond interactions that coexist in the same complex. The following conclusions can be drawn from the present study. It was found that both types of interactions have an enhancement effect on each other, i.e. there is a positive cooperative effect between the anion- π and Pn-bond interactions. This is confirmed by geometric and energetic parameters. A comparison of the E_{coop} values reveals that the cooperative effects are more important in the $P \cdots N$ than $P \cdots O$ interactions. Moreover, weaker Pn-bonds show a larger increased percentage of the interaction energy due to stronger anion- π interaction. The calculated CT values in the anion- π and Pn-bond interactions of the anion- π -Pn systems are slightly greater than those in the isolated complexes, which implies strengthening of the both types of interactions. Meanwhile, the calculated E_{coop} results are in good agreement with the geometric, QTAIM, and CT properties of the complexes.

Supporting Information. Supplementary data associated with this article can be found in the attached *Supporting Information.doc* file.

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Figure 1. Schematic representation and molecular electrostatic potentials of π -acidic heteroaromatic rings **1–4**, PH_2F and PH_2Cl molecules.

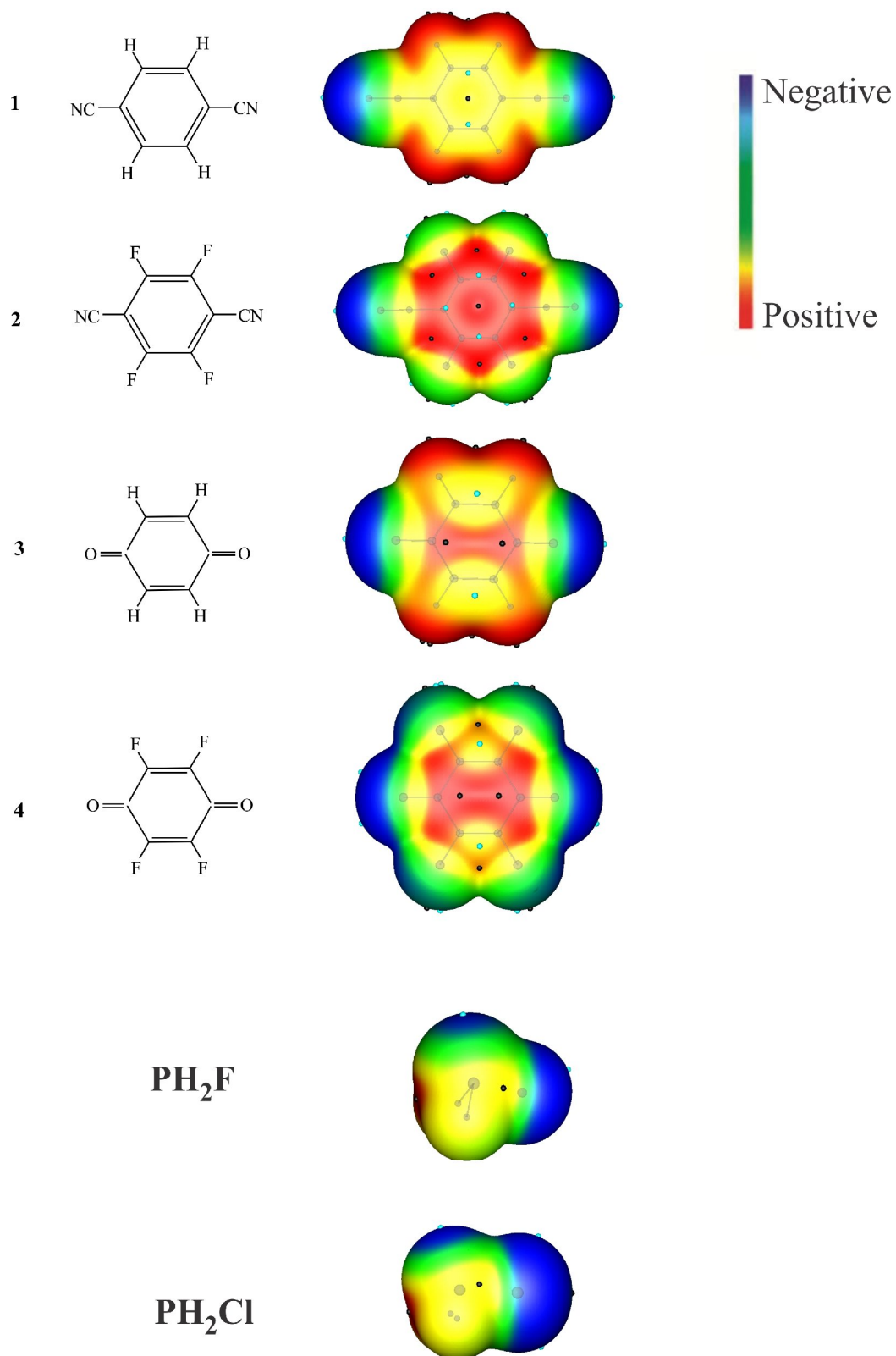


Figure 2. Schematic representation of anion- π complexes **5–12**, pnictogen bond complexes **13–20**, and anion- π -Pn complexes **21–36**. The hydrogen atoms of benzene ring are hidden for simplicity.

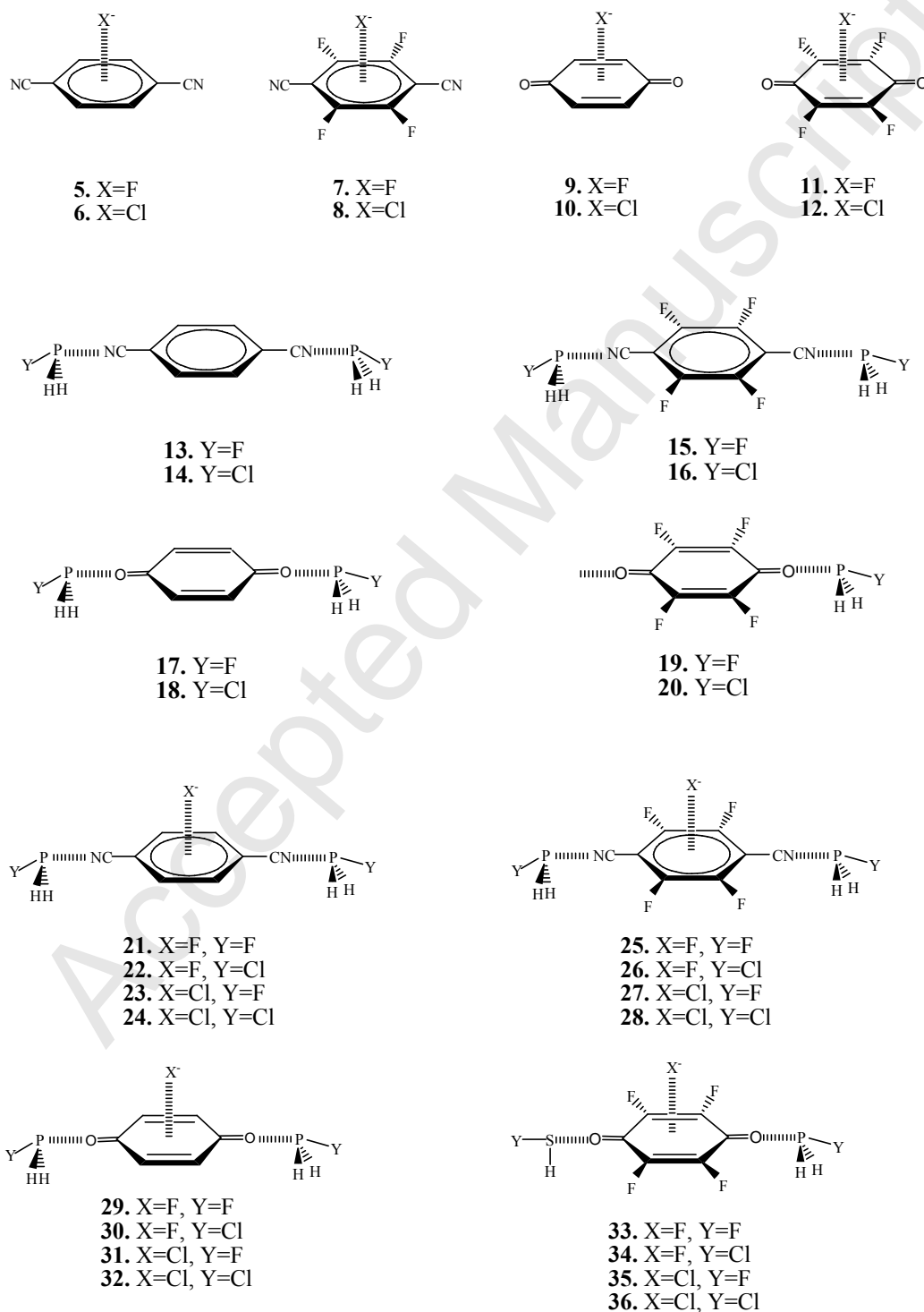


Figure 3. Correlation between cooperative energy and Pn-bond distance change in anion- π -Pn systems

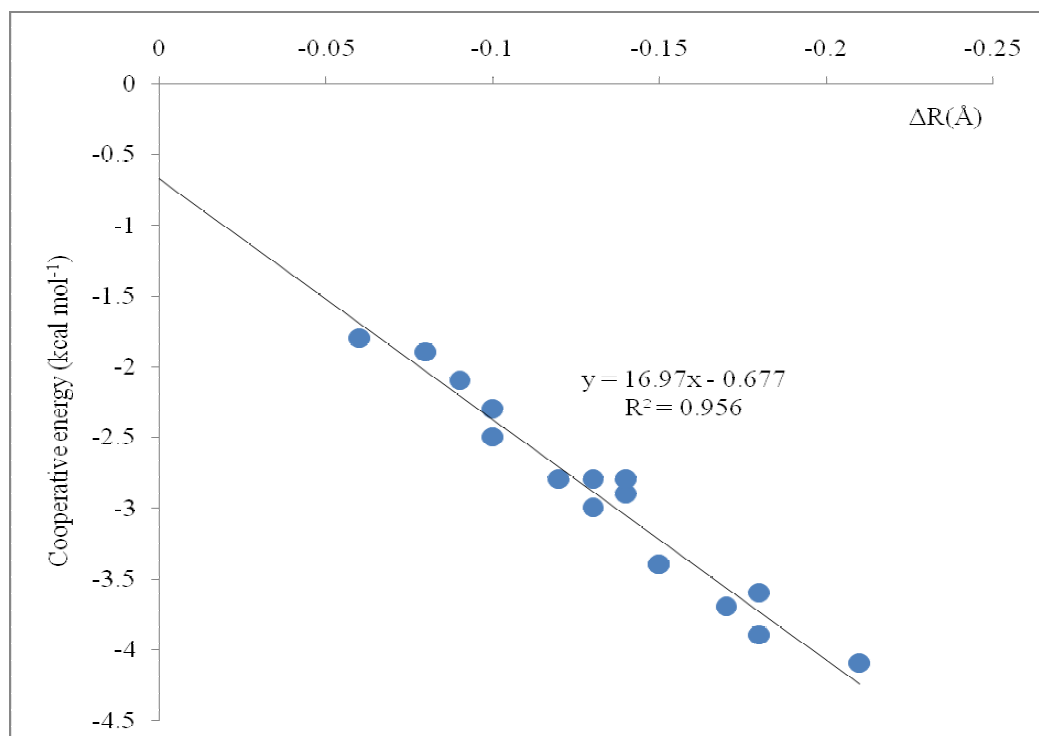


Table 1. Interaction energies, cooperative energies (in kcal mol⁻¹), intermolecular distances and their change ΔR (in Å) for complexes **21-36**

system		E_{int}	E_{coop}	$R_{\text{anion}-\pi}$	$\Delta R_{\text{anion}-\pi}$	$R_{\text{Pn-bond}}$	$\Delta R_{\text{Pn-bond}}$
21	1 +F ⁻ +2PH ₂ F	-29.6	-3.4	2.54	-0.09	2.65	-0.15
22	1 +F ⁻ +2PH ₂ Cl	-28.9	-3.6	2.54	-0.09	2.69	-0.18
23	1 +Cl ⁻ +2PH ₂ F	-24.9	-2.8	3.12	-0.08	2.67	-0.13
24	1 +Cl ⁻ +2PH ₂ Cl	-24.1	-2.9	3.12	-0.08	2.73	-0.14
25	2 +F ⁻ +2PH ₂ F	-42.1	-3.0	2.40	-0.08	2.68	-0.13
26	2 +F ⁻ +2PH ₂ Cl	-41.4	-3.9	2.38	-0.10	2.68	-0.18
27	2 +Cl ⁻ +2PH ₂ F	-33.7	-2.5	2.96	-0.07	2.71	-0.10
28	2 +Cl ⁻ +2PH ₂ Cl	-32.9	-3.4	2.94	-0.09	2.71	-0.15
29	3 +F ⁻ +2PH ₂ F	-33.0	-3.7	2.12	-0.09	2.69	-0.17
30	3 +F ⁻ +2PH ₂ Cl	-33.1	-4.1	2.10	-0.11	2.72	-0.21
31	3 +Cl ⁻ +2PH ₂ F	-22.9	-2.1	3.04	-0.07	2.77	-0.09
32	3 +Cl ⁻ +2PH ₂ Cl	-22.7	-2.3	3.04	-0.07	2.83	-0.10
33	4 +F ⁻ +2PH ₂ F	-47.3	-2.8	2.00	-0.08	2.76	-0.12
34	4 +F ⁻ +2PH ₂ Cl	-47.2	-2.8	2.00	-0.08	2.83	-0.14
35	4 +Cl ⁻ +2PH ₂ F	-32.4	-1.8	2.79	-0.06	2.82	-0.06
36	4 +Cl ⁻ +2PH ₂ Cl	-32.3	-1.9	2.79	-0.06	2.89	-0.08

Table 2. The most positive ($V_{S,max}$, kcal mol⁻¹) and most negative ($V_{S,min}$, kcal mol⁻¹) electrostatic potentials calculated on the surface of molecular electron density at the 0.001 electrons Bohr⁻³ of the monomers (**1–4**) and anion- π complexes (**5–12**)

system		$V_{S,max}$	$V_{S,min}$
1		35.0	-33.4
2		38.4	-26.6
3		28.5	-33.0
4		45.6	-22.4
5	1 +F ⁻	-	-92.0
6	1 +Cl ⁻	-	-87.9
7	2 +F ⁻	-	-85.7
8	2 +Cl ⁻	-	-82.4
9	3 +F ⁻	-	-77.1
10	3 +Cl ⁻	-	-65.9
11	4 +F ⁻	-	-58.4
12	4 +Cl ⁻	-	-87.6

Table 3. QTAIM properties (in au) and amount of charge-transfer (in e) for complexes **21-36**

system		ρ_{RCP}	ρ_{BCP}	$\text{CT}_{\text{anion-}\pi}$	$\text{CT}_{\text{Pn-bond}}$
21	1+F⁻+2PH₂F	0.022	0.017	0.012	0.024
22	1+F⁻+2PH₂Cl	0.021	0.017	0.011	0.038
23	1+Cl⁻+2PH₂F	0.020	0.016	0.010	0.031
24	1+Cl⁻+2PH₂Cl	0.020	0.015	0.009	0.025
25	2+F⁻+2PH₂F	0.020	0.016	0.020	0.014
26	2+F⁻+2PH₂Cl	0.019	0.015	0.018	0.016
27	2+Cl⁻+2PH₂F	0.018	0.015	0.018	0.028
28	2+Cl⁻+2PH₂Cl	0.019	0.014	0.017	0.032
29	3+F⁻+2PH₂F	0.019	0.015	0.052	0.012
30	3+F⁻+2PH₂Cl	0.018	0.016	0.050	0.016
31	3+Cl⁻+2PH₂F	0.018	0.014	0.026	0.010
32	3+Cl⁻+2PH₂Cl	0.018	0.014	0.024	0.012
33	4+F⁻+2PH₂F	0.017	0.013	0.078	0.009
34	4+F⁻+2PH₂Cl	0.017	0.014	0.075	0.010
35	4+Cl⁻+2PH₂F	0.016	0.012	0.052	0.008
36	4+Cl⁻+2PH₂Cl	0.016	0.013	0.050	0.009