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Multi-Center Covalency: Revisiting the Nature of Anion- π Interactions[†]

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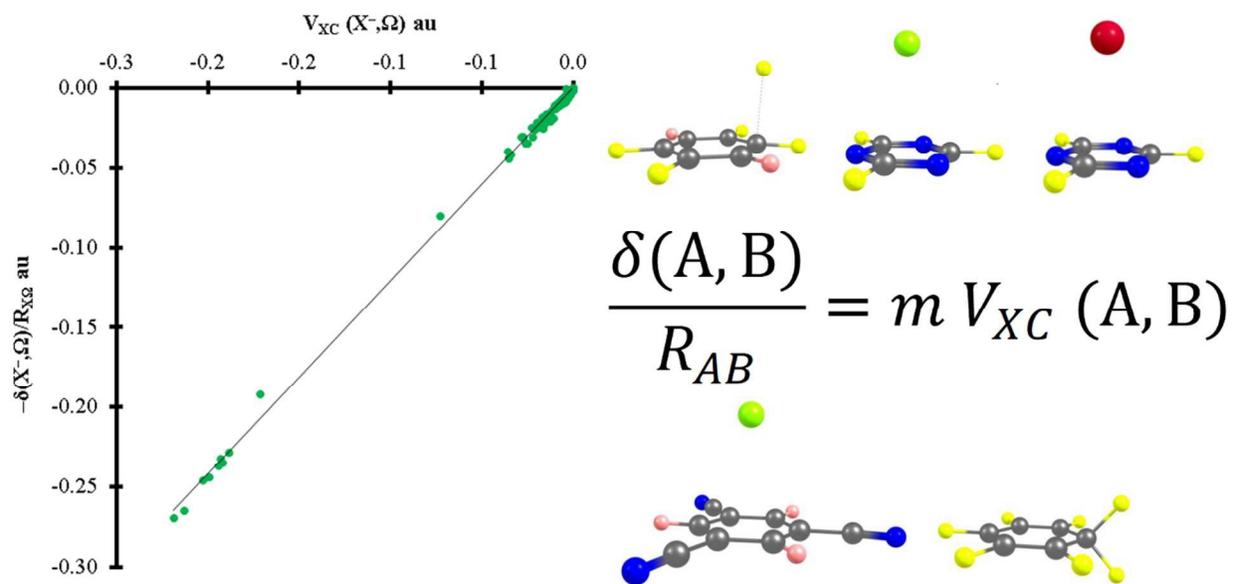
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[†] Electronic Supporting Information (ESI) available: Fig. S1: bonding molecular orbitals of selected complexes. Fig. S2: structures of complexes with atom-numbering scheme. Tab. S1: delocalization indices, electrostatic and exchange-correlation contributions to binding energy. See DOI:

Graphical Abstract



Plot of the delocalization index, $\delta(X^-, \Omega)$, scaled by the internuclear distance $R_{X\Omega}$ versus the exchange-correlation potential $V_{xc}(X^-, \Omega)$ for anion- π complexes

Abstract

Exploring the nature of anion- π bonding by means of the Quantum Theory of Atoms in Molecules (QTAIM) and an energy decomposition scheme on the basis of Interacting Quantum Atoms (IQA) theory led us to conclude that these non-classical interactions benefit from “*multi-center covalency*” far more than from the electrostatics. Comparing to a number of closely related covalent anion- σ complexes reveals that the anion- π systems benefit from an extensive degree of electron sharing between the anions and all atoms of the π -rings. Besides, decomposition of the binding energy into classical (electrostatics) and non-classical (exchange-correlation) components demonstrates that in contrast to previous reports, the anion- π complexes are local minima, if and only if *the non-classical contribution to binding energy surpasses that of the electrostatics*. This suggests that the stable anion- π complexes with the anions atop the π -rings might be prepared with π -systems that benefit more from the exchange-correlation term, such as extended π -systems, but not with strong electrostatic π -receptors. This conclusion is in line with the tendency of strong π -acids to form the σ -complexes with more covalent character instead of the π -complexes.

Keywords

Chemical Bond; Quantum Theory of Atoms in Molecules; Interacting Quantum Atoms; Exchange-Correlation; Anion- π Bonding; Multi-Center Covalency.

1. Introduction

The concepts of *chemical bond*¹ and *covalency*² are the most substantial elements of chemistry, which have remained challenging after 149 and 99 years since the ground-breaking proposals by Frankland and Lewis, respectively.^{3,4} Formation of the covalent bonds between atoms of the same type is inconceivable on the basis of the classical electrostatics. Slater in a pioneering contribution described variation of the kinetic and the potential energies during the bond formation process.⁵ According to his work when two atoms are far from their equilibrium bonding distance, extension of the electronic cloud prior to the bond formation increases the potential energy of the system by attenuating the electron-nucleus attraction but lowers the kinetic energy of the delocalized electrons as they occupy a larger space. The variation of the kinetic energy, which is easily understandable from a simple particle in a box model, is the *first* driving force of the covalent-bond formation. While the bond formation proceeds, the kinetic energy of the system increases due to a significant confinement of the electrons between two atoms but the potential energy of the system drops by a strong electrostatic interaction between the *shared* electrons and the nuclei of the newly formed molecule. Meanwhile, electron exchange and correlation play an important role in decreasing the potential energy by reducing the electron-electron repulsion.⁵ Altogether, the decrease in the potential energy is always more than the increase in the kinetic energy, as anticipated from the virial theorem, and lowers the total electronic energy of the *bonded atoms*, i.e. the molecule. Unlike the ionic (electrostatic) bonding that is easy to understand in terms of classical electrostatics, understanding the covalency needs a heedful treatment of the quantum-mechanical effects, i.e. exchange and correlation besides the kinetic energy in the formation of a covalent bond.

Nevertheless, the physical explanation by Slater does not provide a chemical insight towards the nature of the covalent bond. Therefore, numerous chemical theories are developed for decomposing the energy or charge density of a molecular system into the individual terms that are paralleling the *chemical concepts*.⁶⁻¹⁵ In the hierarchy of chemical-bond theories, the Quantum Theory of Atoms in Molecules (QTAIM)¹⁶ and the theory of Interacting Quantum Atoms (IQA)¹⁷⁻²⁰ incorporating the QTAIM partitioning scheme are distinguished because of analyzing electron density, a real-space property, and being free of any arbitrary reference state.

In general, various chemical-bond theories distinguish strong covalent and ionic bonds easily. However, when it comes to the realm of intermolecular interactions, where the border between the covalency and the ionicity is blurry, distinguishing the weight of the quantum and classical contributions to the bond energy and classification of the bond type is not a trivial task. Careful examinations of weak bonds have several times demonstrated that allegedly “non-covalent” interactions benefit from significant degrees of covalency.²¹⁻²³

In the present work we reconsider the nature of anion- π interactions in the light of quantum chemical topology approaches and demonstrate how to recover chemically meaningful information from the physical terms.²⁴⁻²⁶ The anion- π interactions constitute a class of intermolecular interactions between anions and π -rings often functionalized with electron-withdrawing substituents or electronegative heteroatoms.²⁷⁻³⁴ There is a general consensus in the chemical community about the *non-covalent* nature of the anion- π interactions. This conclusion was drawn on the basis of the relatively low electron density at the critical points of the QTAIM^{30,31,33} between the anions and the π -system as well as small overlap between molecular/atomic orbitals of the anions and those of the π -systems.³⁵ Diverse factors such as dispersion, induction, polarization, and pure electrostatics have been suggested to be the driving

force for the formation of the anion- π complexes.³⁶⁻⁴¹ Comprehensive reviews on the nature and applications of the anion- π complexes have been published in recent years and have listed the abovementioned stabilizing factors.⁴²⁻⁵⁷

Our preliminary studies on the nature of ion- π interactions suggest that the anion- π complexes benefit from a non-negligible degree of *electron sharing* between anions and the π -systems.⁵⁸ In the present contribution we examine a set of anion- π complexes ranging from weak to strongly-bonded systems and compare them with covalently-bonded anionic σ -complexes used as our reference systems. The main objective of this work is to characterize the *magnitude of electron sharing* between halides and the π -systems and *quantify* the role of electron sharing in terms of components of binding energy. Further, we partition the binding energy into two terms; *classical* (electrostatic energy) and *quantum* or *non-classical* (kinetic energy, and exchange-correlation energy) components according to the IQA convention.¹⁷⁻²⁰ Decomposition of the binding energy demonstrates why simple electrostatic models^{40,41} are successful in recovering the binding energy of the anion- π complexes, despite the fact that these systems benefit significantly from an inter-fragment electron sharing or *multi-center covalency*.

In the rest of the manuscript in Section 2.1 we carefully discuss the conceptual connection between the covalency and electron sharing defined within the context of the QTAIM. In Section 2.2 we analyze the energetic aspects of anion- π interaction within the context of IQA theory and study the relationships between the electronic and energetic criteria of bonding. Our concluding remarks are summarized in Section 3 and in the Section 4 all schemes and methods used in this study are presented.

2. Results and Discussions

2.1 Electron Sharing and Covalency

Among various energy/charge partitioning schemes, QTAIM provides one of the most straightforward characteristics of electron sharing that can be used for defining the *covalency and bond order*. The idea of covalency and bond order within the context of QTAIM originates from the definition of the bond order in Mulliken population analysis. According to the IUPAC definition the bond order is defined as the *total* orbital overlap population between a pair of atoms.⁵⁹ In QTAIM, this quantity is called *delocalization index*, $\delta(A,B)$, and can be calculated between any pair of atoms like *A* and *B* in a molecule or a supramolecular complex.⁶⁰⁻⁶⁵ Among various definitions of the delocalization index a conceivable definition of the DI can be given with respect to the fluctuation of basin population.⁶⁶ One can show that the delocalization index provides a covariance of the joint probability distribution for the number of electrons in the basins of atoms *A* and *B* as the following:

$$\delta(A, B) = -2cov(n_A, n_B) = -2[\langle n_A n_B \rangle - \langle n_A \rangle \langle n_B \rangle] \quad \text{Equation 1}$$

In **Equation 1** $\langle n_A n_B \rangle = \sum_{n_A, n_B} n_A n_B p(n_A, n_B)$ and $\langle n_A \rangle = \sum_{n_A} n_A p(n_A)$ where $p(n_A, n_B)$ and $p(n_A)$ are electron number distribution functions.⁶² In a nutshell, the delocalization index for every pair of atoms represents the number of electrons that do not belong to neither of atomic basins exclusively but are shared between them. This picture is consistent with the notion of covalency.⁶¹

It is worth noting that in addition to the conceptual discussion, given above, recent studies^{67,68} have demonstrated that the delocalization index satisfies the expectations of a covalency index in the field of nuclear magnetic shielding as it has been predicted before.⁶⁹

Employing the delocalization index as a sum of the overlap of *all* pairs of orbitals for our model systems, **Figure 1**, ensures that even slightest contribution of each single orbital is considered, **Tables 1 and S1**; whereas analyzing the molecular orbitals (MO) depicted at an arbitrarily chosen iso-surface value or checking the coefficients of selected MOs does not guarantee recovering the *total* electron sharing that is the bond order according to the IUPAC definition, **Figure S1**.

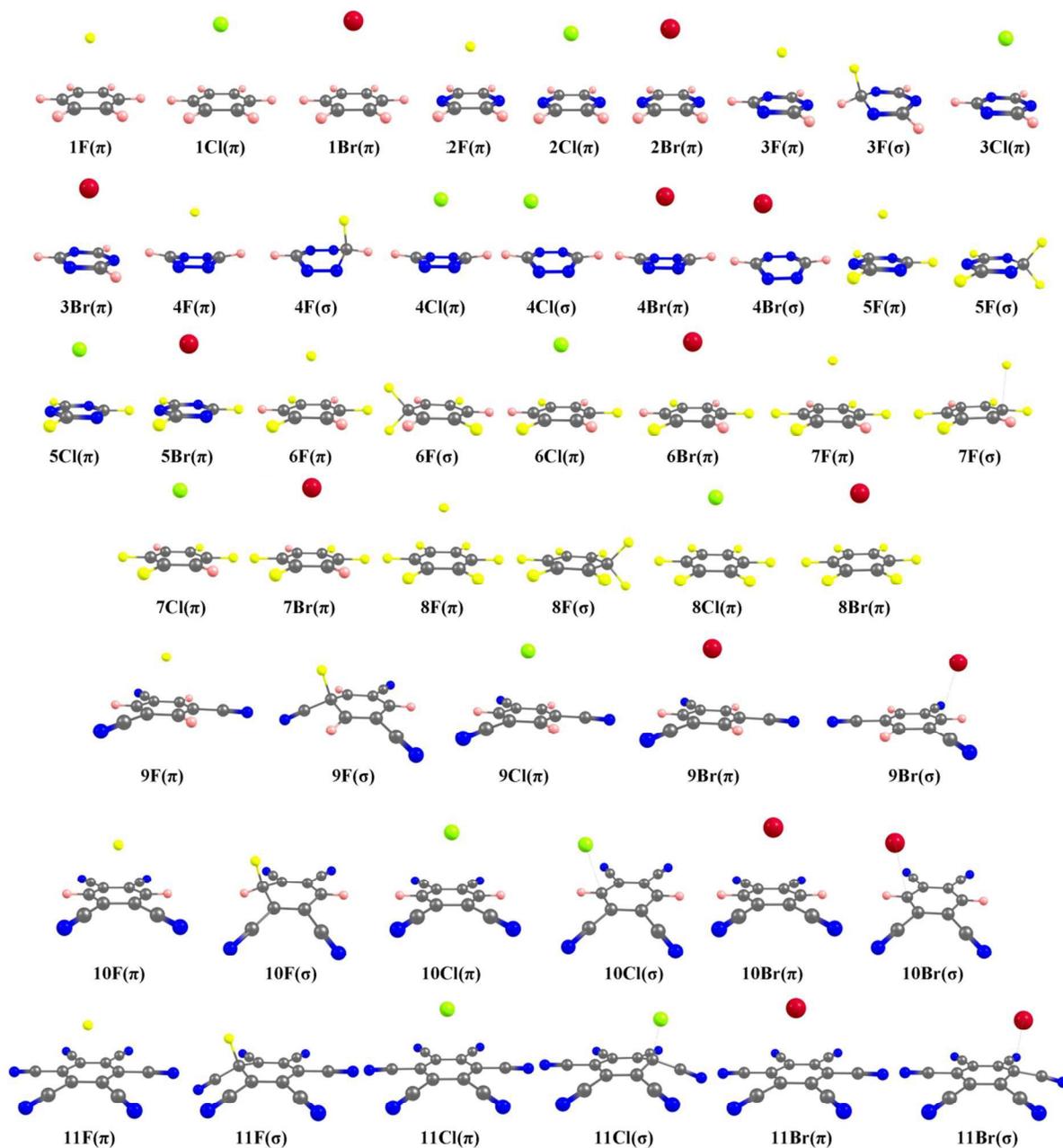


Figure 1. Structures of complexes studied in the present work; numbers below each structure represent the following π -systems **1**: benzene, **2**: 1,4-diazine, **3**: 1,3,5-triazine, **4**: 1,2,4,5-tetrazine, **5**: 2,4,6-trifluoro-1,3,5-triazine, **6**: 1,3,5-trifluorobenzene, **7**: 1,2,4,5-tetrafluorobenzene, **8**: hexafluorobenzene, **9**: 1,3,5-tricyanobenzene, **10**: 1,2,4,5-tetracyanobenzene, and **11**: hexacyanobenzene. Complexation with fluoride, chloride or bromide is denoted by F, Cl, or Br in the name of complex and the Greek letter in the parenthesis defines the type of complex, i.e., π -complex or σ -complex.

Table 1. The magnitude of the delocalization indices in atomic units between halides and different parts of the π -systems; $\delta(X, Mol)$ represents the total inter-fragment number of electrons that each halide is sharing with the π -system. The number of electrons that are shared between the halide and the interior of the π -ring, i.e., the sp^2 atoms, is denoted by $\delta(X, \pi)$. The $\delta(X, C_\sigma)$ value represents the number of *pairwise* electron sharing between the halides and the directly-bonded carbon atom of the π -ring in σ -complexes. The electron sharing between the halide and the leaving group, i.e., the substituent on the carbon covalently bonded to the halide in σ -complexes, is presented by $\delta(X, lg)$. Finally, $\delta(X, res)$ characterizes the total electron sharing between the halides and the rest of atoms of the systems; numbers listed in regular font represent the electron sharing between the anions and the substituents whereas italic numbers for σ -complexes represent that for the anions and the atoms of the interior of the ring.

Complex	$\delta(X, Mol)$	$\delta(X, \pi)$	$\delta(X, C_\sigma)$	$\delta(X, lg)$	$\delta(X, res)$	Complex	$\delta(X, Mol)$	$\delta(X, \pi)$	$\delta(X, C_\sigma)$	$\delta(X, lg)$	$\delta(X, res)$
1F(π)	0.182	0.174			0.008	7F(π)	0.276	0.252			0.024
1Cl(π)	0.164	0.155			0.009	7F(σ)	0.417		0.131	0.078	0.033 <i>0.175^a</i>
1Br(π)	0.174	0.161			0.013	7Cl(π)	0.266	0.233			0.033
2F(π)	0.270	0.262			0.008	7Br(π)	0.271	0.234			0.037
2Cl(π)	0.242	0.231			0.011	8F(π)	0.307	0.275			0.032
2Br(π)	0.242	0.229			0.013	8F(σ)	1.124		0.664	0.179	0.081 <i>0.200^a</i>
3F(π)	0.293	0.286			0.007	8Cl(π)	0.310	0.262			0.048
3F(σ)	1.083		0.644	0.077	0.003 <i>0.359^a</i>	8Br(π)	0.314	0.259			0.055
3Cl(π)	0.257	0.248			0.009	9F(π)	0.335	0.304			0.031
3Br(π)	0.253	0.243			0.010	9F(σ)	1.124		0.654	0.146	0.024 <i>0.300^a</i>
4F(π)	0.415	0.403			0.012	9Cl(π)	0.323	0.283			0.040
4F(σ)	1.093		0.648	0.071	0.002 <i>0.372^a</i>	9Br(π)	0.325	0.280			0.045
4Cl(π)	0.365	0.350			0.015	9Br(σ)	0.493		0.168	0.053	0.085 <i>0.187^a</i>
4Cl(σ)	0.423		0.129	0.032	0.002 <i>0.260^a</i>	10F(π)	0.356	0.319			0.037
4Br(π)	0.362	0.345			0.017	10F(σ)	1.116		0.720	0.070	0.055 <i>0.271^a</i>
4Br(σ)	0.388		0.104	0.024	0.003 <i>0.257^a</i>	10Cl(π)	0.349	0.301			0.048
5F(π)	0.359	0.334			0.025	10Cl(σ)	0.569		0.201	0.048	0.088 <i>0.232^a</i>
5F(σ)	1.112		0.607	0.170	0.007 <i>0.328^a</i>	10Br(π)	0.355	0.301			0.054
5Cl(π)	0.329	0.296			0.033	10Br(σ)	0.532		0.168	0.044	0.191 <i>0.129^a</i>
5Br(π)	0.325	0.289			0.036	11F(π)	0.397	0.347			0.050
6F(π)	0.256	0.236			0.020	11F(σ)	1.175		0.724	0.136	0.060 <i>0.255^a</i>
6F(σ)	1.116		0.659	0.177	0.033 <i>0.251^a</i>	11Cl(π)	0.396	0.326			0.070
6Cl(π)	0.246	0.219			0.027	11Cl(σ)	1.342		0.730	0.163	0.114 <i>0.335^a</i>
6Br(π)	0.253	0.222			0.031	11Br(π)	0.403	0.324			0.079
						11Br(σ)	1.040		0.385	0.164	0.136 <i>0.355^a</i>

a. The delocalization between halides and the rest of atoms in the interior of π -rings in σ -complexes is realized through both π - and σ -type orbitals just like for the $\delta(X, \pi)$ values, but the weight of σ -type increases significantly by formation of a σ -covalent bond. Therefore these values are not listed as $\delta(X, \pi)$ values.

Before discussing the delocalization index as an index of bond order one must note a subtle issue that stems from the *chemical conventions*. In fact, the magnitude of the electron sharing for a homopolar bond is different from that of heteropolar bonds.⁷⁰ A heteropolar covalent bond has a

lower electron sharing but instead, the difference in the charges of neighboring atoms strengthens the bond by an additional electrostatic attraction. For instance, although, everyone accepts that carbon-carbon bond in ethane and carbon-fluorine bonds in tetrafluoromethane are both single covalent bonds, the magnitude of the delocalization index for the homopolar C–C bond is 1.01 *au* whereas that for the heteropolar C–F is just 0.57 *au* (computed at M06-2X/def2-TZVPPD computational level). Therefore, it is essential to compare the delocalization index of any system of interest with a *proper reference system* according to the *chemical convention*. It is necessary to note that magnitude of the delocalization index for a particular system varies at various computational levels. Accordingly, one must calibrate the bond-order values with respect to the computational level as well.⁶¹

In the present work, the reference systems for defining the covalency of the anion- π bonds are the anion- σ -complexes that have been classified as being weak to strong covalently bonded.^{35,71}

For the anion- π systems, the extent of the covalency can be defined relative to the magnitude of the pairwise electron sharing of the halide-carbon bond in the anion- σ -complexes, $\delta(\mathbf{X}, \mathbf{C}_\sigma)$, **Table 1**. The minimum and maximum values obtained for the weak to strong σ X–C single covalent bonds are **0.131–0.724 *au***, (F–C), **0.129–0.730 *au***, (Cl–C), and **0.104–0.385 *au*** (Br–C). The minimum pairwise electron-sharing values for the halide-carbon σ -bonds are comparable with those of the so-called covalent hydrogen bonds.⁷²⁻⁷⁴

The magnitude of the electron sharing between the anions and the π -systems, $\delta(\mathbf{X}, \boldsymbol{\pi})$, for all studied complexes lies in the middle of the range of a normal X–C covalent bond. Although the pairwise electron sharing between the anions and individual atoms of the ring is relatively small for the anion- π complexes, because the halide is simultaneously interacting with six atoms in a ring, the overall electron sharing is significant. Therefore, this type of interaction belongs to

multi-center interactions with a significant contribution of covalency. It is not surprising that when a single atom interacts with multiple atoms by a covalent-type mechanism, pairwise electron sharing reduces significantly and the bond lengths for each individual atom-atom interaction increases. This also explains why no substantial charge concentration (expected for the pairwise covalency)^{30,31,33,35,71} is observed between the halides and the carbon/nitrogen atoms of the aromatic rings; the longer the bond, the lower the charge concentration in-between the bonded atoms.

Considering the electron sharing index as a measure of the covalency suggests that the nature of the anion- π interactions is similar to that of an ordinary single covalent bond, but electronic indices do not suffice for understanding the energetic factors that are responsible for a bond formation. In particular, electronic indices cannot demonstrate *to what extent electron sharing influences the energy of a bond*. In the following Section 2.2 we discuss the energetic factors behind the formation of an anion- π complex.

2.2 Covalency of the Anion- π Bonding from the Energy Perspective

There are two questions, one can ask about the covalency of the anion- π bonding. First, if the anion- π bonding has a covalent contribution, how does the covalency affect the bond energy?

Second, why are simple electrostatic models successful in recovering the bond energy?

These questions can be addressed using the theory of Interacting Quantum Atoms, IQA.¹⁷⁻²⁰ The IQA energy-decomposition scheme breaks the molecular energy down into the atomic (or self) and interatomic (bond) contributions. The bond energy further decomposes to nucleus-nucleus, nucleus-electron, and electron-electron, contributions. The electron-electron contribution itself is composed of two parts: (a) Coulombic electron-electron repulsion and (b) quantum

mechanical exchange-correlation stabilization. One can write the IQA binding energy, E_{Bind} , as the following:

$$E_{Bind} = V_{El} + V_{XC} + E_{Pr} \quad \text{Equation 2}$$

The first term V_{El} is the sum of the nucleus–nucleus, nucleus–electron, and *Coulombic* electron–electron contributions to the binding energy; this term is conventionally called the *electrostatic* or *classical* contribution.¹⁷⁻²⁰ The electrostatic contribution for two interacting fragments can be either positive (repulsive) or negative (attractive). The second term V_{XC} defines the pure contribution of the non-classical factors to the binding energy, i.e. exchange and correlation. The exchange-correlation contribution is always negative but its magnitude varies substantially for various systems. The last term E_{Pr} in **Equation 2**, the preparation energy, is the energy required for reorganizing the electron distribution in an atom/fragment to prepare it for the bond formation. It has been demonstrated that, as it is expected from the virial theorem,⁵ the preparation energy reflects the increase in the kinetic energy of a system and is always positive for covalent bonding.²² The preparation energy may also include the deformation energy of a fragment (E_{Def}), if the reference system for the binding energy comprises the equilibrium geometries of the fragments before bond formation. In the present work the preparation energy includes exclusively the electronic part (for more information, see **Methods** Section 4). The IQA energy-decomposition scheme has a unique advantage; it does not invoke any arbitrary reference state or non-physical term for evaluating the components of the binding energy.

In a series of papers Pendás et. al. have demonstrated that the exchange-correlation energy of the IQA is a good measure of covalent-type interactions. Indeed, the formulation of the exchange-

correlation term is closely related to that of the electron sharing, the delocalization index.^{75,76}

Recently, the exchange-correlation component has been suggested as the energy descriptor of the covalency.⁷⁷ **Table 2** summarizes the IQA energy terms for the systems **1F–11Br**.

Table 2. Binding energy and IQA energy components (in kJ/mol); \mathbf{BE}_{DFT} and \mathbf{E}_{Def} represent the binding energy obtained from DFT computations and the deformation energy that is the energy required to change the equilibrium geometry of a free π -system to its geometry in a complex, respectively. \mathbf{BE}_{IQA} , $V_{\text{El}}(\mathbf{X}, \mathbf{Ar})$, $V_{\text{XC}}(\mathbf{X}, \mathbf{Ar})$, $V_{\text{XC}}(\mathbf{X}, \pi)$, and $V_{\text{XC}}(\mathbf{X}, \mathbf{C}_\sigma)$ are the IQA binding energy, electrostatic potential energy between the halide and all atoms of Ar system, exchange-correlation potential energy between the halide and all atoms of Ar system, exchange-correlation energy between the halide and the interior atoms of the π -ring, and the pairwise exchange-correlation energy for the σ -bond in σ -complexes, respectively. The $\%V_{\text{XC}}$, $\mathbf{E}_{\text{Pr}}(\mathbf{X})$, $\mathbf{E}_{\text{Pr}}(\mathbf{Ar})$, and \mathbf{NImF} are the percentage of exchange-correlation contribution $V_{\text{XC}}(\mathbf{X}, \mathbf{Ar})$ in the sum $V_{\text{El}}(\mathbf{X}, \mathbf{Ar}) + V_{\text{XC}}(\mathbf{X}, \mathbf{Ar})$, the preparation energy for the halide, the preparation energy for the π -system, and the number of imaginary frequencies for each structure, respectively.

Complex	\mathbf{BE}_{DFT}	\mathbf{E}_{Def}	\mathbf{BE}_{IQA}	$V_{\text{El}}(\mathbf{X}, \mathbf{Ar})$	$V_{\text{XC}}(\mathbf{X}, \mathbf{Ar})$	$V_{\text{XC}}(\mathbf{X}, \pi)$	$V_{\text{XC}}(\mathbf{X}, \mathbf{C}_\sigma)$	$\%V_{\text{XC}}$	$\mathbf{E}_{\text{Pr}}(\mathbf{X})$	$\mathbf{E}_{\text{Pr}}(\mathbf{Ar})$	\mathbf{NImF}
1F(π)	0.6	1.1	2.1	-24.0	-64.6	-64.5		72.92	19.9	70.8	2
1Cl(π)	2.9	0.9	4.8	0.4	-51.1	-49.9		---^a	17.0	38.4	2
1Br(π)	2.8	0.8	4.7	-1.5	-50.2	-50.1		97.10	15.6	40.8	2
2F(π)	-37.3	2.7	-36.8	-68.7	-107.3	-105.4		60.98	37.7	101.4	1
2Cl(π)	-20.9	1.7	-20.1	-18.4	-82.8	-80.4		81.84	28.0	53.1	1
2Br(π)	-18.3	1.5	-17.6	-11.9	-78.5	-76.5		86.86	22.6	50.2	1
3F(π)	-56.8	2.2	-56.6	-91.9	-121.6	-85.0		56.94	43.2	113.8	2
3F(σ)	-265.0	124.7	-266.7	-391.1	-684.0		-503.8	63.62	393.3	415.1	0
3Cl(π)	-32.3	1.0	-32.1	-28.9	-91.0	-89.0		75.89	29.6	58.3	0
3Br(π)	-27.9	0.8	-27.9	-20.4	-85.0	-83.2		80.68	23.2	54.3	0
4F(π)	-107.7	21.0	-108.6	-126.0	-178.0	-176.2		58.56	70.1	125.3	1
4F(σ)	-298.0	131.3	-297.9	-412.2	-691.7		-510.7	62.66	398.2	407.7	0
4Cl(π)	-64.3	12.2	-65.1	-42.2	-132.8	-128.8		75.88	46.9	63.0	1
4Cl(σ)	-64.5	11.1	-65.4	-34.8	-153.5		-60.3	81.52	58.7	64.1	0
4Br(π)	-56.7	11.1	-57.8	-28.5	-124.9	-120.8		81.41	38.9	56.7	1
4Br(σ)	-56.1	10.1	-57.0	-23.0	-133.0		-45.0	85.25	43.5	55.5	0
5F(π)	-120.4	5.9	-118.6	-161.2	-157.3	-106.7		49.40	61.3	138.7	2
5F(σ)	-486.6	230.9	-487.1	-628.8	-744.7		-507.8	54.22	496.9	389.4	0
5Cl(π)	-74.9	2.5	-74.6	-66.8	-123.0	-114.4		64.8	40.6	74.6	0
5Br(π)	-65.9	1.9	-66.3	-48.4	-115.5	-106.1		70.45	32.2	65.5	0
6F(π)	-45.2	2.0	-41.2	-80.2	-100.9	-97.8		55.71	35.2	104.7	1
6F(σ)	-290.8	184.2	-293.1	-489.5	-717.7		-523.7	59.45	441.5	472.6	0
6Cl(π)	-29.0	1.2	-24.2	-30.7	-84.2	-78.2		73.66	28.3	61.7	0
6Br(π)	-26.1	1.1	-21.2	-21.2	-82.6	-76.1		79.61	23.7	59.0	0
7F(π)	-60.1	1.7	-54.7	-97.7	-110.9	-106.6		53.16	40.3	113.7	2
7F(σ)	-71.2	5.4	-73.0	-109.7	-177.5		-74.3	61.81	73.9	140.4	0
7Cl(π)	-40.0	1.0	-34.9	-39.7	-92.3	-84.8		69.95	30.9	66.2	0
7Br(π)	-36.2	0.9	-31.3	-27.8	-90.3	-81.6		76.47	25.6	61.2	0
8F(π)	-90.5	1.8	-83.8	-134.5	-127.9	-121.5		48.76	49.8	128.8	2
8F(σ)	-302.5	166.7	-303.6	-485.7	-728.2		-532.1	59.99	435.4	474.8	0

8Cl(π)	-62.7	0.8	-55.8	-60.1	-110.5	-99.7		64.77	38.1	76.7	0
8Br(π)	-57.1	0.7	-50.6	-42.5	-106.9	-93.6		71.57	31.3	67.5	0
9F(π)	-123.7	1.0	-121.1	-185.9	-139.5	-134.4		42.87	55.7	148.7	2
9F(σ)	-248.9	94.6	-249.8	-356.6	-666.2		-495.4	65.13	349.9	423.2	0
9Cl(π)	-88.6	1.0	-86.1	-96.5	-115.9	-106.8		54.48	40.7	86.0	0
9Br(π)	-81.0	1.0	-78.7	-78.3	-111.4	-100.7		58.71	33.2	77.8	2
9Br(σ)	-86.9	2.2	-87.9	-53.1	-162.9		-72.8	75.42	62.3	65.7	0
10F(π)	-155.6	1.1	-151.3	-225.2	-150.6	-144.0		40.06	61.8	162.7	2
10F(σ)	-372.6	110.7	-374.3	-526.1	-706.4		-559.3	57.31	421.7	436.5	0
10Cl(π)	-113.1	1.2	-111.8	-121.5	-126.9	-115.9		51.9	45.0	91.6	1
10Cl(σ)	-120.8	3.1	-123.0	-87.2	-200.6		-95.4	69.69	88.3	76.5	0
10Br(π)	-103.8	1.2	-102.9	-100.7	-123.1	-110.6		55.01	37.8	83.1	1
10Br(σ)	-108.5	2.4	-110.8	-68.8	-175.6		-74.9	71.85	69.4	64.2	0
11F(π)	-216.0	0.8	-213.5	-302.4	-172.9	-163.1		36.37	74.9	187.0	2
11F(σ)	-463.8	121.1	-467.1	-603.0	-746.6		-574.0	55.32	454.3	428.2	0
11Cl(π)	-159.1	0.8	-155.2	-171.4	-147.3	-130.1		46.22	54.0	109.4	2
11Cl(σ)	-263.4	86.3	-265.2	13.7	-630.1		-449.9	<u> </u> ^a	330.7	25.5	0
11Br(π)	-146.4	0.9	-143.2	-142.3	-143.1	-123.6		50.14	45.2	96.9	2
11Br(σ)	-180.6	25.3	-183.7	-24.3	-366.0		-192.3	93.78	191.0	15.6	0

a. In these cases the contribution of the electrostatics in the binding energy is positive (repulsive); accordingly, the proportion of the exchange-correlation term to the sum of $V_{EI}(X,Ar)$ + $V_{XC}(X,Ar)$ is more than 100 percent.

Comparing the percentage of the exchange-correlation contribution in the anion- π systems with that for various σ -complexes confirms the conclusion drawn from the electron-sharing index. A higher contribution from exchange-correlation energy component compared to the electrostatics demonstrates significance of non-classical factors in anion- π bonding. Plotting the exchange-correlation potential energy versus the delocalization index demonstrates the applicability of the V_{XC} to be used as an indicator of the bond covalency, **Figure 2**. A linear equation can be fitted to the plot of the exchange-correlation energy versus the delocalization index either for the anion- π systems or by extending the correlation to include the σ -complexes. Although, the slope of the linear correlation changes by inclusion of σ -complexes, the correlation coefficient remains considerably high, which suggests that the systems benefit from very similar type of interaction for the stabilization.

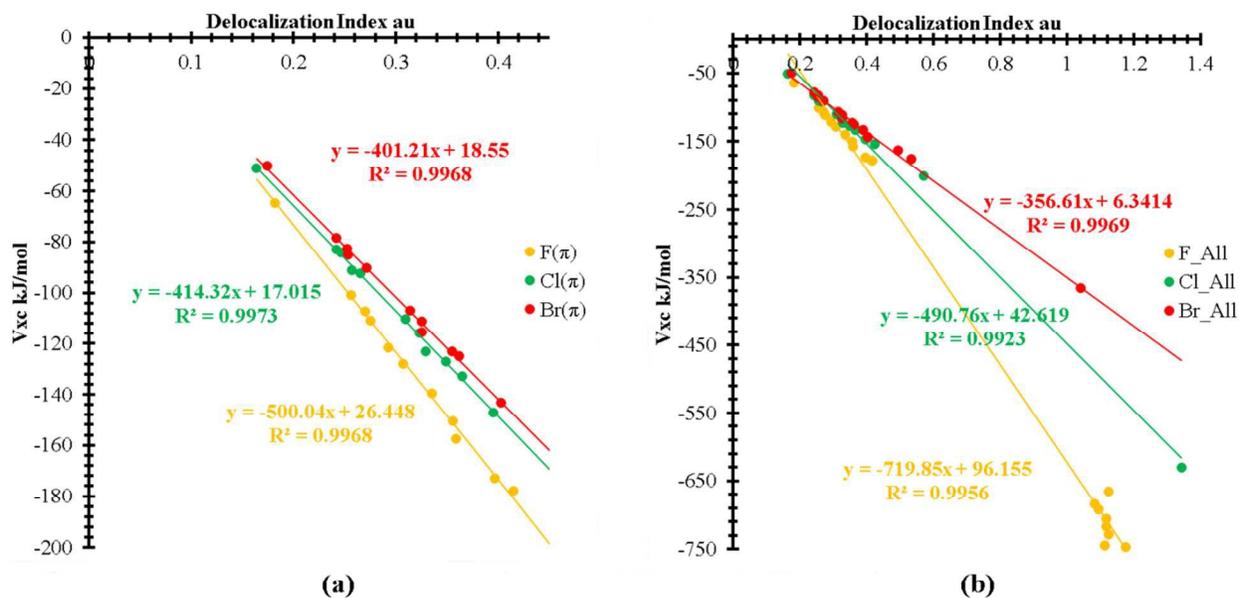


Figure 2. Plot of total (inter-fragment) exchange-correlation potential energy, $V_{XC}(X,Ar)$, versus the total inter-fragment delocalization index, $\delta(X,Ar)$; (a) the regression line is just delineated for the anion- π complexes, and (b) for all complexes (including σ -complexes).

Different slopes for the plots of the delocalization index versus the exchange-correlation energy for various compounds, **Figure 2**, originate from the difference of the bond lengths in various halide- π complexes. Popelier and Rafat⁷⁸ suggested that the delocalization index, **Equation 3**, can be linked to the exchange-correlation potential, **Equation 4**, to a first order approximation by **Equation 5**.

$$\delta(A,B) = 2|\iint[\rho_2^{AB}(\mathbf{r}_1, \mathbf{r}_2) - \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)]d\mathbf{r}_1d\mathbf{r}_2| \quad \text{Equation 3}$$

$$V_{XC}(A,B) = \iint[\rho_2^{AB}(\mathbf{r}_1, \mathbf{r}_2) - \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)]r_{12}^{-1}d\mathbf{r}_1d\mathbf{r}_2 \quad \text{Equation 4}$$

$$\frac{\delta(A,B)}{R_{AB}} = m V_{XC}(A,B) \quad \text{Equation 5}$$

Plotting the exchange-correlation contribution for every single atom versus the delocalization index, scaled by the inter-nuclear distance, proves the validity of this assumption and the relation between the electronic and energetic criteria of bonding within the context of QTAIM and IQA theories, **Figure 3**.

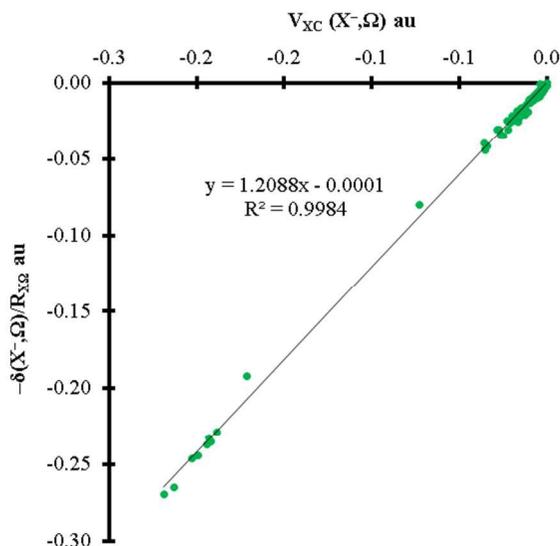


Figure 3. Plot of the delocalization index scaled by the inter-nuclear distance versus the exchange-correlation potential energy for halide anions and different atoms in the π -systems; as it is expected from **Equation 5** a linear equation with negligible intercept can be fitted into the plot.

Comparing the relative contributions of the classical and non-classical factors in the binding energy suggests that in majority of the complexes the exchange-correlation is the *main driving force* of the bond formation (see **Table 2**). Only in very strong anion- π complexes the magnitude of the electrostatics surpasses that of the exchange-correlation. Interestingly, these complexes with relatively low exchange-correlation contribution (**F(π)** complexes and **10/11X(π)** complexes) *are not local minima* on their Potential-Energy hyper-Surfaces (PES) and convert to the σ -complexes with a higher contribution of the exchange-correlation term, i.e., more covalent character.

Plotting the exchange-correlation and electrostatic contributions versus the total binding energy for the anion- π (Figure 4a) as well as all complexes (Figure 4b, including σ -complexes) demonstrates the significant role of the exchange-correlation term in stabilizing the weak and moderate anion- π complexes as well as the σ -complexes. Nevertheless, the plots of the $V_{XC}(X,Ar)$ and $V_{EI}(X,Ar)$ versus the binding energy deviate from linearity because neither the exchange-correlation nor the electrostatics are the sole factors defining the magnitude of the binding energy.

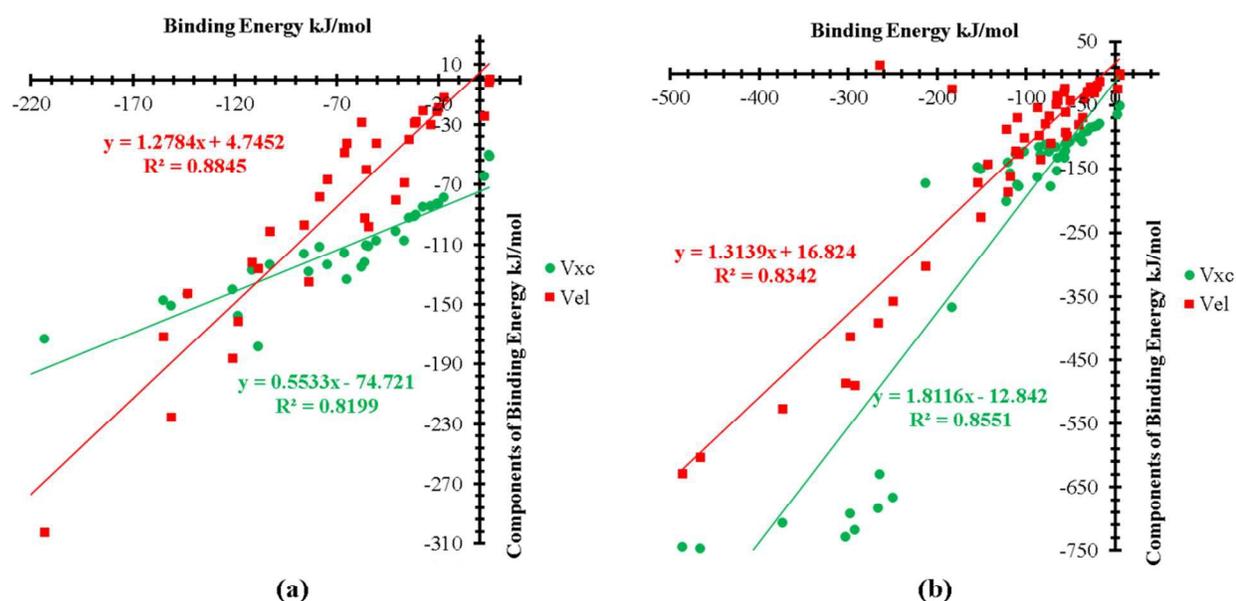


Figure 4. Plots of the binding energy versus the exchange-correlation potential energy, $V_{XC}(X,Ar)$ (green circles), and the electrostatic potential energy, $V_{EI}(X,Ar)$ (red squares) for (a) anion- π complexes and (b) all systems (including σ -complexes).

In spite of the significant contribution of the non-classical term, previous studies did not appreciate the role of this factor for anion- π complexes. This can be understood concerning the nature of the methods that were used for probing the anion- π interactions. In fact, as it has been

discussed by Pendás et. al.²² conventional energy decomposition (ED) schemes generally do not distinguish between the contributions of the kinetic energy and exchange-correlation term, which lowers the potential energy. ED methods usually provide merely an exchange-repulsion term, which is an amalgam of the kinetic energy, the exchange-correlation energy, and even Coulombic contribution. Accordingly, a large portion of the exchange-correlation contribution vanishes in such type of analysis. Unfortunately, other terms that are obtained from the conventional ED schemes, for example, orbital interaction or charge-transfer, are also composed of several contributions. Therefore, interpretations of such schemes are different from that based on IQA.²²

The IQA energy decomposition reveals that an unfavorable increase in the preparation energy originating from the *kinetic* term is the main source of the repulsion in the anion- π interactions. The magnitude of this non-classical effect is virtually comparable with that of the exchange-correlation contribution for local minimum structures (for both the anion- π and σ -complexes). Accordingly, the decrease in the *potential energy* because of the exchange-correlation contribution is obliterated by the increase in the *kinetic energy*. Therefore, any probe that characterizes the electrostatic contribution can recover the binding energy with an acceptable accuracy. However, one must note that a hypothetical probe, built for measuring the sole effect of the exchange-correlation contribution, can estimate the binding energy too, because the preparation energy overshadows the electrostatics in the similar manner as it does for the exchange-correlation. In particular, one must note that the trends in the variation of the electrostatics and the exchange-correlation contribution are the same among all studied series. It is worth emphasizing that one cannot simply rule out the contribution of the exchange-correlation assuming that the magnitude of the inter-fragment exchange-correlation energy and

preparation energies are comparable. Indeed, the magnitude of the preparation energy is greater than that of the exchange-correlation energy for strongly covalent “ σ -complexes” and some ordinary σ -bonds.⁷⁹ However, conventionally –and legitimately– the C–X bonds in the σ -complexes are considered as covalent because of their short bond lengths and high-electron density between the halides and π -systems.

High preparation energies for the fluoride- π complexes compared to those for the chloride- π and bromide- π systems reflect the fact that the fluoride must approach more closely towards the π -system to form the covalent bond. However, with the fluoride in close proximity of the π -system, the electron densities of both interacting fragments disturb and the kinetic energy elevates substantially. As a result, the fluoride- π complexes are not local minima on their PES. On the other hand, the chloride- π and bromide- π complexes are more stable as the preparation energy does not elevate much during their bond-formation processes. Furthermore, unlike the fluoride- π , the chloride- π and bromide- π complexes benefit from a relatively higher exchange-correlation contribution that is consistent with the lower electronegativity and higher polarizability of the chlorine and bromine atoms.

Besides the preparation energy, the deformation energy (E_{Def}), which originates from the reorganization of the equilibrium geometries of the π -systems to the geometries of the π -systems in the anion- π complexes, is another source of the energy increase. Although unfavorable, the deformation energy for the π -complexes is quite negligible in comparison with their significant preparation energies. In contrast, the deformation energies are considerably larger for the σ -complexes, where a planar sp^2 carbon transforms to a tetrahedral sp^3 carbon.

3. Conclusions

In the present account we revisited the nature of the anion- π complexes in the light of quantum chemical topology approaches; QTAIM and IQA. The QTAIM has been one of the first methods employed for characterizing the nature of the anion- π bonds.^{30,31,33} However, unfortunately the QTAIM analysis remained limited to the topological analysis, i.e., studying the characteristics of the critical points of the electron density, which is somewhat controversial part of the theory.⁶³ Employing the QTAIM, in the current work we focused on characterizing the extent of electron sharing between the anions ($X = F^-$, Cl^- , Br^-) and various π -systems on the basis of the inter-fragment delocalization index. Because the DI varies with polarity of individual bonds and the theoretical level,⁶¹ it should be compared with references of known bond types at a similar computational level. In the present work, we compared the delocalization indices for selected anion- π systems with those of the formerly identified covalent anion- σ -complexes. The analysis demonstrated that the delocalization indices of our anion- π systems are comparable with those of the covalent σ -complexes. Although the magnitude of the electron sharing between the anions and the individual atoms in a π -ring is relatively small (~ 0.03 to 0.06 au), comparable with a weak hydrogen bond,⁸⁰ the number of all shared electrons between the anions and the π -systems (0.16 to 0.35 au) is significantly larger than that for a conventional non-covalent interaction, with a typical electron sharing of ~ 0.10 au. As a result we propose that anion- π complexes benefit from a *multi-center covalency*.

To validate this hypothesis, the IQA energy-decomposition analysis was employed. The relative contributions of the classical (electrostatic) and non-classical (exchange-correlation) components of the binding energy confirm that the larger contribution arises from the non-classical part, which has been assigned to the covalency.⁷⁵⁻⁷⁸ Interestingly, the anion- π complexes with low proportion of the exchange-correlation component –fluoride- π complexes and halide- π

complexes with highly electron-withdrawing substituents— are not local minima on their potential-energy surfaces. This suggests that for experimental preparation and isolation of an anion- π complex, a large π -system, for example a polyaromatic hydrocarbon or graphene flakes are probably more promising than the aromatics with highly electron-withdrawing substituents.⁵⁸ Indeed, in the π -rings with highly electronegative substituents, anion- π complexes collapse and form σ -complexes that benefit more from the exchange-correlation contribution as a result of their pairwise covalent bonds. This feature explains why anion- π complexes with anions atop the π -rings have rarely been identified in experiments;⁷¹ this might originate in an inappropriate selection of anion receptors, with strong electrostatic potentials but poor exchange-correlation abilities.

4. Methods

Eleven π -systems known as weak to strong π -acceptors were selected and their complexes with fluoride, chloride, and bromide were fully optimized. Local minima were identified by checking the eigenvalues of the hessian matrix of energy. Besides, for obtaining the anion- π complexes with anions atop the center of π -rings, several structures were optimized for finding first and second order saddle points. All structures with anions interacting with either the π -systems or forming σ -complexes were selected but structures with anions interacting with hydrogens (hydrogen-bond complexes) were excluded from further analysis. All computations were performed at M06-2X⁸¹/Def2-TZVPPD⁸² computational level by Gaussian 09, rev D02 suite of programs.⁸³ The binding energies of the complexes were defined with respect to the free anions and the geometries of the π -systems in the complexes. The energy difference between the equilibrium geometries of the free π -systems and that of the complexed ones are reported as the

deformation energies, **Table 2**. Binding energies were computed at the same computational level.

QTAIM and IQA analyses were performed by using AIMAll, version 15.05.18.⁸⁴ The accuracy of QTAIM computations was checked by measuring the energy error during the integration. Atomic properties including delocalization indices were computed by means of proaim and promega-1st order integration procedures implemented in AIMAll. The error in IQA analysis as a result of the inherent inaccuracy of the second-order density matrix of DFT is between 0.0 to 6.5 kJ/mol and the average of the absolute values of errors is 2.2 kJ/mol.

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