A DFT investigation of anion-π interactions between halogen oxyanions (XO₃⁻, X = Cl, Br, I) and aromatic π-systems (benzene and coronene)

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Abstract. Anion-π interactions have proved to play a key role in many chemical and biochemical phenomena. In order to investigate the nature and the applications of these interactions, the anion-π interactions of the chlorate (ClO₃⁻), bromate (BrO₃⁻), and iodate (IO₃⁻) oxyanions with benzene and coronene have been studied using density functional theory (DFT). The structures, adsorption energies, and electronic properties of XO₃⁻ (X = Cl, Br, I) adsorbed on benzene and coronene have been explored using dispersion corrected DFT hybrid functional, M06-2X-D3, with the def2-TZVP basis set. Benzene and coronene have been respectively used as a building block and a simple flake of graphene. The interaction of these anions with benzene is found to be unexpectedly favorable. Their binding strength is further increased when the anions are adsorbed on coronene. Moreover, energy decomposition analysis based on symmetry adapted perturbation theory (SAPT) has been performed and the nature of interaction is characterized using noncovalent interaction analysis (NCI) based on reduced density gradient (RDG) method. Generally, the favorable binding of these anions with benzene or coronene is mainly ascribed to dispersion interactions. These anion-π interactions with graphene flakes or with benzene can be utilized in the design of anions receptors and detectors.

1. Introduction
Noncovalent interactions have proved to be of great influence in various chemical and biological applications [1-4]. One of these interactions is the anion-π interaction that has attracted significant attention theoretically [5-10] and experimentally [11-13]. Because of the essential role of anions in biological and chemical systems and their connection to environmental pollution, anion recognition has grown as an important research area. Since there are many ways to bind anions (hydrogen bonding, electrostatic, etc.) [14], the design of neutral anion receptors using aromatic rings is a recent promising research field [15-16].
The previous theoretical studies have been focused on understanding the nature of interaction between anions and simple electron-deficient aromatic systems (e.g., substituted benzene). Generally, it has been believed that electrostatic interactions between aromatics with positive quadrupole moment ($Q_{zz}$) and anions, as well as induction are the dominant forces in these types of interactions [8]. In another study, it has been demonstrated that the binding of anions is mainly due to the interactions with the dipoles induced by the ring substituents [9-10]. Despite what is expected of the repulsion between anions and electron-rich aromatic systems (with negative $Q_{zz}$), it has been reported that the polarizability of the benzene substituents causes a favorable interaction between halides and substituted benzene [17-19]. Because the previous studies were more concentrated on the interaction between halides and substituted benzene, here in this study the interaction of polyatomic oxyanions namely: chlorate ($\text{ClO}_3\text{‾}$), bromate ($\text{BrO}_3\text{‾}$), and iodate ($\text{IO}_3\text{‾}$) with unsubstituted benzene is investigated, where their binding is unexpectedly found favorable. Furthermore, a new adsorbent; coronene (which is a simple flake of graphene) is introduced to improve the anion-$\pi$ binding by making use of its large unoccupied $\pi$ orbitals. In recent years, graphene has been recognized as an emerging nanomaterial with exceptional properties and wide applications in technology [20-23]. These flakes can be used in the removal of toxic anions like arsenite, arsenate, phosphate, etc. as expected by previous experimental results [24-26]. Also, several theoretical studies [27-37] have been performed to investigate the adsorption of anions on graphene or graphene-based materials.

To the best of our knowledge, the adsorption of the trigonal pyramidal anions ($\text{ClO}_3\text{‾}$, $\text{BrO}_3\text{‾}$, and $\text{IO}_3\text{‾}$) on benzene and coronene has never been studied so far. However, these oxyanions are toxic and unsafe for living organisms [38-39]. For instance, bromate is a possible carcinogen, highly soluble in water and it is difficult to be removed using conventional methods [40]. So, it is important to design a receptor for these kind of anions. In this study, we aim to carefully study the interactions of the above mentioned anions with benzene and with the larger surface area coronene. Understanding the nature of anion-$\pi$ interaction has helped in utilizing them in anion recognition [41-42], and in the design of anion receptors [43-45].

2. Computational details

In order to investigate the adsorption of the 3 oxyanions; chlorate ($\text{ClO}_3\text{‾}$), bromate ($\text{BrO}_3\text{‾}$), and iodate ($\text{IO}_3\text{‾}$) on benzene and coronene surfaces, M06-2X-D3/def2-TZVP level of DFT theory is used. It was found that M06-2X has broader accuracy than other popular DFT functionals when studying noncovalent interactions [46]. Although M06-2X has medium-range electron correlation to some extent [47], adding the D3 version of Grimme’s dispersion correction [48] to account for long-range electron correlation has proven to improve its results in noncovalent interactions [49]. It has also been verified that def2-TZVP [50] basis set provides accurate results for noncovalent interactions involving anions without the need of adding diffuse functions [51]. Effective potentials were used for the core electrons of the iodine atom [52]. Geometry optimization and frequency calculations were done using Gaussian09 package [53]. All molecular structures were optimized without any symmetry constraints and with the default convergence parameters. Vibrational frequency analysis was carried out at the same level of theory to verify the stability of each complex. Depending on the position and orientation of each oxyanion on every adsorbent, the complexes change from local minima to first or even second-order saddle points. Adsorption energy $E_{ads}$ is obtained as the difference between the total calculated energies of the complex and its interacting species using the following expression:

$$E_{ads} = E_{\text{complex}} - E_{\pi\text{-system}} - E_{\text{XO}_3\text{‾}}$$

where $E_{\text{complex}}$ is the total energy of the optimized adsorbed system, $E_{\pi\text{-system}}$ is the energy of the $\pi$-system ($C_6H_6$ and $C_{24}H_{12}$), and $E_{\text{XO}_3\text{‾}}$ is the energy of the isolated anion where (X = Cl, Br, I). Due to the resulted
basis set superposition error (BSSE), all calculated adsorption energies were corrected using the counterpoise method [54].

To analyze and understand the nature of the intermolecular orbital interactions between the oxyanions and the studied adsorbents, natural bond orbital (NBO) analysis was employed [55-56]. Furthermore, interaction energy decomposition analysis of the low-energy complexes of chlorate and bromate was carried out using the symmetry-adapted perturbation theory (SAPT) [57-59]. The total interaction energy is decomposed into electrostatic (E_{elst}), exchange-repulsion (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) components. sSAPT0 has been chosen along with the def2-TZVP basis set. sSAPT0 is a wavefunction-based SAPT method that provides the best error by unit computational effort [60]. SAPT calculations were performed using PSI4 software [61]. Moreover, NCI analysis based on the reduced density gradient (RDG) method [62] has been carried out using Multiwfn program [63]. This analysis has helped in visualizing and characterizing the studied anion-π interactions.

3. Results and discussion

3.1. Structures and adsorption energies of C₆H₆–XO₃⁻ and C₂₄H₁₂–XO₃⁻ (X = Cl, Br, I) complexes

Here, the adsorption of the three halogen oxyanions (ClO₃⁻, BrO₃⁻, IO₃⁻) on benzene and coronene is carefully explored. The calculated geometrical structures of XO₃⁻ (X = Cl, Br, I) in gas phase and in adsorbed phase are listed in table 1. It is worth noting that the M06-2X-D3 bond lengths (r_{X–O}) and bond angles (\angle O–X–O) are in reasonable agreement with the corresponding previously reported experimental values [64-66]. As shown in table 1, the bond angles are 0.99%–3.74% larger than the experimental parameters while the bond lengths are approximately similar to the experimental values. As in experiment, the M06-2X-D3 optimized geometries show that r_{X–O} bond length gets longer when going from ClO₃⁻ (1.480 Å) to IO₃⁻ (1.785 Å). On adsorption, the oxyanions are not geometrically changed significantly, which is consistent with physisorption. For example, the change in the bond angles upon adsorption is ~ 0.07-0.33 (deg) with respect to the calculated parameters in the gas phase.

| Anions | Gas phase | Adsorbed phase |
|--------|-----------|----------------|
| ClO₃⁻  |           |                |
| r_{Cl–O} (Å) | 1.480 [64] | 1.480 | 1.481 | 1.480 |
| \angle O–Cl–O (deg) | 106.60 [64] | 107.66 | 107.73 | 107.80 |
| BrO₃⁻  |           |                |
| r_{Br–O} (Å) | 1.640 [65] | 1.637 | 1.638 | 1.637 |
| \angle O–Br–O (deg) | 105.5 [65] | 106.72 | 106.81 | 106.65 |
| IO₃⁻   |           |                |
| r_{I–O} (Å) | 1.790 [66] | 1.785 | 1.786 | 1.785 |
| \angle O–I–O (deg) | 102.0 [66] | 105.81 | 105.71 | 105.48 |

The optimized structures of the low-lying energy conformers of C₆H₆–XO₃⁻ complexes are shown in figure 1, together with the corresponding adsorption energies (E_{ads}) in kJ/mol and the equilibrium distance between the X-atom of the anion and the ring centroid (z), R_{X–z}. Because our present goal is to analyze the nature of the interaction between the halogen oxyanions and the π-system of the electron-rich benzene.
Figure 1. Optimized structures of the C_{6}H_{6}XO_{3}^{-} (X = Cl, Br, I) complexes calculated at the M06-2X-D3/def2-TZVP level with BSSE correction. Down and Up mean downward and upward orientations of the halogen atom. Adsorption energies (E_{ads} in kJ/mol) and R_{X-z} equilibrium distances (Å) between the ring centroid z and the anion halogen atom X are given.

and coronene rings, we only considered two low-lying energy conformers of the C_{6}H_{6}XO_{3}^{-} complexes indicated by X-Up and X-Down as depicted in figure 1. In both conformers, the anions are located along the z-axis of the benzene ring with the halogen atoms perpendicularly located above the benzene centroid. The oxygen atoms in each of these conformers can have staggered tripod orientation in which they are stacked on the midpoint of the C=C bonds (\angle O-X-z-C dihedral angle d = 30°) or they can have an eclipsed orientation in which the oxygen atoms are stacked on the C atoms (d = 0°). Both orientations of oxygen atoms are nearly isoenergetic, so only the staggered conformations are considered here. All benzene complexes are characterized by second-order saddle points with two or three imaginary frequencies (ranging from \sim 20.0i to 60.0i), which originate from the X–O swings toward the H-atoms as the anions prefer hydrogen bonding rather than binding to the \pi-ring [67]. Careful inspection of the data given in figure 1 shows that the X- Down conformers are more favorable than the corresponding X-Up ones. The adsorption energies of the X-Down (X-Up) conformers are -1.82 (2.80), -3.72 (1.54), and -5.84 kJ/mol (-0.75 kJ/mol) for ClO_{3}^{-}, BrO_{3}^{-}, and IO_{3}^{-}, respectively. This unfavorable binding of the X-Up conformers can be explained on the basis that the negatively charged oxygen atoms in these conformers are pointed toward the benzene ring, and hence the repulsive electrostatic interaction between
the oxyanions and the negative quadrupole moment of benzene ($Q_{zz} = -8.7 \pm 0.5 \text{ DÅ}$ [68]) is maximized. As noticed, there is an increase in the binding strength as going from ClO$_3^-$ to IO$_3^-$, which can be related to the corresponding decrease in the anions electronegativity. However, the equilibrium distances ($R_{X-z}$) increase when going from ClO$_3^-$ (3.159 Å) to BrO$_3^-$ (3.269 Å) and to IO$_3^-$ (3.446 Å). This behavior can be assigned to the steric effect that increases as the size of the halogen atom increases and thus the oxyanion is pushed a little farther from the benzene surface.

Different orientations and positions were studied for the trigonal pyramidal anions on coronene and the conformers are shown in figure 2, with geometrical and energetic properties summarized in table 2. Three adsorption sites were considered: Top (T), Bridge (B), and Hollow (H) sites with respect to the halogen atom.

![Figure 2](image_url)

**Figure 2.** Optimized structures of the different conformers of C$_{24}$H$_{12}$–ClO$_3^-$ complexes calculated at the M06-2X-D3/def2-TZVP level. The same conformers are studied for both C$_{24}$H$_{12}$–BrO$_3^-$ and C$_{24}$H$_{12}$–IO$_3^-$ complexes.
distances increases with increasing the halogen size. The adsorption energies for the most stable complexes, the binding strength increases as the halogen electronegativity decreases and the equilibrium order: Down-H(0˚) < Up-H(30˚) complexes depends on the sites and orientations the adsorbed anions adapt, which follows the following E2 values in table 3 are the sum of the energies from individual contributions related to the dominant interaction and is mainly dispersion in nature as will be discussed later in the SAPT section. The reported favourable binding in oxyanions-benzene complexes lack of any contribution of donor-acceptor interaction and is mainly dispersion in nature. However, there are more than one stable conformer for the H site: Down-H(0˚), Up-H(0˚), Up-H(30˚), and Up-H(130˚). In contrast to C6H6-XO3̅, X-Up orientations are more stable than the X-Down orientations, see table 2. This finding suggests that there is an interaction between the oxygen atoms and the C-C orbitals. However, XO3̅‾ is more stable than the Down geometry when adsorbed on electron deficient aromatic rings [45, 69]. Among the Up conformers, T site is the most stable one with oxygen atoms interacting with the centers of the rings, where there is depletion in the electron density. Moreover, XO3̅‾ (X = Cl, Br, I) anions form much more stable complexes when adsorbed on T site at the edge of the coronene with a difference of 3.19, 4.90, and 6.53 kJ/mol with respect to the corresponding T site (center) complexes, respectively. All the optimized geometries of the T-conformers are minima, while those of the B-conformers have one small imaginary frequency that corresponds to a transition state of the corresponding T-conformer. On the other hand, H-conformer geometries have 2 or 3 imaginary frequencies (< 40i) for Up-H(0˚) and Up-H(30˚), given that Up-H(0˚) is slightly more stable than Up-H(30˚) by 0.24-0.53 kJ/mol. Overall, the stability of the studied complexes depends on the sites and orientations the adsorbed anions adapt, which follows the following order: Down-H(0˚) < Down-H(30˚) < Up-H(30˚) < Up-H(0˚) < B < T < T-edge. Similar to benzene complexes, the binding strength increases as the halogen electronegativity decreases and the equilibrium distances increases with increasing the halogen size. The adsorption energies for the most stable conformers are −25.11 (ClO3̅‾), −26.83 (BrO3̅‾), and −28.01 kJ/mol (IO3̅‾). In order to understand the nature of the anion-π interaction, NBO analysis was performed on all the local minima complexes at the same level of calculation. The NBO charge transfer (ΔQ) from the anions to the coronene is calculated and compiled in table 3 as well as the second order perturbation energies (E2) resulting from the second order perturbation analysis of Fock matrix in the NBO basis. The analysis shows a stabilization due to the interaction between the lone pair orbitals (LP) of the oxygen atoms in the oxyanions and the anti-bonding σ* C–C orbitals. However, ΔQ and E2 are relatively lower in C6H6-XO3̅‾ complexes, compared to C24H12-XO3̅‾. This finding may conclude that the favourable binding in oxyanions-benzene complexes lack of any contribution of donor-acceptor interaction and is mainly dispersion in nature as will be discussed later in the SAPT section. The reported E2 values in table 3 are the sum of the energies from individual contributions related to the dominant

| Adsorption site | ClO3̅‾ | BrO3̅‾ | IO3̅‾ |
|----------------|-------|-------|-------|
|                | E_ads | R_Cl-z | E_ads | R_Br-z | E_ads | R_I-z |
| Down-H(0˚)     | −3.81 | 2.943 | −0.27 | 3.102 | −0.46 | 3.373 |
| Down-H(30˚)    | −3.95 | 2.949 | −0.36 | 3.102 | −0.51 | 3.373 |
| Up-H(0˚)       | −13.72 | 3.506 | −14.54 | 3.576 | −14.56 | 3.667 |
| Up-H(30˚)      | −13.29 | 3.507 | −14.01 | 3.576 | −14.32 | 3.660 |
| B              | −18.25 | 3.524 | −19.02 | 3.603 | −19.68 | 3.709 |
| T              | −21.92 | 3.481 | −21.93 | 3.563 | −21.48 | 3.663 |
| T-edge         | −25.11 | 3.456 | −26.83 | 3.522 | −28.01 | 3.608 |

Since there are a lot of possibilities for the different orientations on each position, only the stable orientations are considered here. For example, the dihedral angle (d) \( \angle O–X–C–C \) in T site can range from 0˚ to 60˚, and it is found that the optimization of all T-conformers with the different d values, whether the halogen atoms are up or down, will lead to only one conformer: X-Up with d = 60˚, so this conformer is referred to as T site. There is only one X-Up orientation of B site, as shown in figure 2.
interaction $\text{LP (O)} \rightarrow \pi^* \text{C–C}$. Inspection of the results in table 3 reveals that as the distance between the oxygen atoms of the interacting oxyanions and the surface of coronene becomes shorter, the $\text{LP (O)} \rightarrow \pi^* \text{C–C}$ interaction increases, causing a subsequent increase in the charge transfer and the donor-acceptor nature, as indicated by the largest $\Delta Q$ and $E^2$ values for $\text{C}_{24}\text{H}_{12}^-\text{ClO}_3^-$.

A comparison between the results of $E_{\text{ads}}$ in table 2 and $E^2$ in table 3 shows that there may be forces other than charge transfer causes the interaction energy to increase when going from $\text{ClO}_3^-$ to $\text{IO}_3^-$; these forces may be of electrostatic and/or dispersion nature as will be shown later. Furthermore, the enhancement in the stability when the oxyanion moves to the edge may be ascribed to an increase in the attractive electrostatic interaction, since the charge transfer decreases at the T-edge for each anion as shown in table 3. Therefore, charge transfer takes part in stabilizing the adsorption process of the oxyanions on coronene.

### Table 3.

| Complex          | $\Delta Q$ | $E^2$ [LP (O) $\rightarrow \pi^* (\text{C–C})$] | $\Delta Q$ | $E^2$ [LP (O) $\rightarrow \pi^* (\text{C–C})$] |
|------------------|------------|-----------------------------------------------|------------|-----------------------------------------------|
| $\text{C}_{24}\text{H}_{12}^-\text{ClO}_3^-$ | 0.031      | 10.92                                        | 0.027      | 10.42                                        |
| $\text{C}_{24}\text{H}_{12}^-\text{BrO}_3^-$ | 0.025      | 9.67                                         | 0.022      | 9.41                                         |
| $\text{C}_{24}\text{H}_{12}^-\text{IO}_3^-$  | 0.028      | 9.50                                         | 0.023      | 9.79                                         |

**Figure 3.** Electrostatic potential map (ESP) of benzene, coronene, and $\text{XO}_3^-$ ($X = \text{Cl, Br, I}$) anions on the 0.001 electrons/bohr$^3$ surfaces obtained at the M06-2X-D3/def2-TZVP level. (C: grey; H: white; Cl: green; Br: dark red; I: purple; O: red)

Inspection of the electrostatic potential map (ESP) of coronene with respect to benzene (figure 3) reveals that there is some relative electron deficiency in the centers of the rings of coronene as represented by the decrease in the intensity of the red color. This verifies that there is a difference
between the anions interaction with coronene and with benzene [31]. In addition, the increase in the relative positive charge density around the halogen atom when going from ClO\textsubscript{3}\textsuperscript{−} to BrO\textsubscript{3}\textsuperscript{−} and to IO\textsubscript{3}\textsuperscript{−} in figure 3 is obvious. According to NBO analysis, the charges on Cl, Br, and I in their isolated anions are respectively +1.819, +2.077, and +2.521, while the negative charges on oxygen atoms are −0.940, −1.026, and −1.174. In agreement with the ESP maps of benzene and coronene, the NBO negative charges on carbons are decreased from −0.212 in benzene to −0.008 (−0.180) in the central ring (edges) of coronene. Accordingly, the binding strength of the studied halogen oxyanions increases when adsorbed on coronene, compared to their adsorption on benzene.

3.2. SAPT analysis of C\textsubscript{6}H\textsubscript{6}–XO\textsubscript{3}\textsuperscript{−} and C\textsubscript{2}4H\textsubscript{12}–XO\textsubscript{3}\textsuperscript{−} (X = Cl, Br) complexes

Table 4 lists the SAPT interaction energies components of the Down complexes of benzene and all the local minima complexes of coronene. This energy decomposition analysis helps in determining the forces that are responsible for the anion–π interactions. As shown in table 4, the calculated interaction energies (E\textsubscript{int}) at M06-2X-D3/def2-TZVP are approximately in agreement with the sSAPT0 total interaction energies (E\textsubscript{tot}). It is found that the electrostatic interaction (E\textsubscript{elst}) in benzene complexes is favourable. Also, E\textsubscript{elst} increases in C\textsubscript{6}H\textsubscript{6}–BrO\textsubscript{3}\textsuperscript{−} by ~7.5 kJ/mol, compared to C\textsubscript{6}H\textsubscript{6}–ClO\textsubscript{3}\textsuperscript{−} complex because of the increase in the nuclear positive charge acquired by the bromine atom in BrO\textsubscript{3}\textsuperscript{−}. The most dominant interaction in benzene complexes is due to the dispersion force (E\textsubscript{disp}), which becomes larger when BrO\textsubscript{3}\textsuperscript{−} is adsorbed due to its larger size (larger polarizability). Careful inspection shows that the anion-induced polarization (E\textsubscript{ind}) has relatively small favorable contributions to the interaction energies of both ClO\textsubscript{3}\textsuperscript{−} and BrO\textsubscript{3}\textsuperscript{−} complexes with benzene. Therefore, trigonal pyramidal anions can interact favorably with electron-rich benzene ring especially when the oxygens are oriented upwards because of the favorable dispersion, induction, and electrostatic forces that compensate for the repulsive exchange forces.

Table 4. sSAPT0/def2-TZVP components for the conformers of C\textsubscript{6}H\textsubscript{6}–XO\textsubscript{3}\textsuperscript{−} and C\textsubscript{2}4H\textsubscript{12}–XO\textsubscript{3}\textsuperscript{−} (X = Cl, Br). The M06-2X-D3/def2-TZVP interaction energies E\textsubscript{int} are also given. All energies are in kJ/mol.

| Complex      | Conformer | E\textsubscript{elst} | E\textsubscript{exch} | E\textsubscript{ind} | E\textsubscript{disp} | E\textsubscript{int} | E\textsubscript{int} |
|--------------|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| C\textsubscript{6}H\textsubscript{6}–ClO\textsubscript{3}\textsuperscript{−} | X-Down    | −0.88                  | 31.53                  | −8.57                  | −25.49                  | −3.41                  | −2.68                  |
| C\textsubscript{6}H\textsubscript{6}–BrO\textsubscript{3}\textsuperscript{−} | X-Down    | −8.35                  | 34.76                  | −5.72                  | −26.55                  | −5.86                  | −4.52                  |
| C\textsubscript{2}4H\textsubscript{12}–ClO\textsubscript{3}\textsuperscript{−} | T         | 11.63                  | 66.77                  | −45.99                 | −62.53                  | −30.12                 | −22.34                 |
|              | T-edge    | 2.91                   | 63.21                  | −44.67                 | −51.60                  | −30.15                 | −26.53                 |
| C\textsubscript{2}4H\textsubscript{12}–BrO\textsubscript{3}\textsuperscript{−} | T         | 11.43                  | 70.18                  | −46.25                 | −68.67                  | −33.31                 | −22.64                 |
|              | T-edge    | 1.18                   | 65.67                  | −44.39                 | −56.39                  | −33.93                 | −28.33                 |

In the case of coronene, the negatively charged oxygen atoms are facing the electron cloud of the flake causing repulsive E\textsubscript{elst} values. There is a relatively small decrease in the repulsive E\textsubscript{elst} when going from C\textsubscript{2}4H\textsubscript{12}–ClO\textsubscript{3}\textsuperscript{−} to C\textsubscript{2}4H\textsubscript{12}–BrO\textsubscript{3}\textsuperscript{−} complex. However, the electrostatic energy decreases substantially to 2.91 (1.18) kJ/mol from 11.63 (11.43) kJ/mol for ClO\textsubscript{3}\textsuperscript{−} (BrO\textsubscript{3}\textsuperscript{−}) when they are adsorbed at the edge of coronene. This lowering in E\textsubscript{elst} is the main reason for the increase in the stability of the anions when adsorbed at the edge, compared to their adsorption in the coronene centroid. The results in table 4 show that the dispersion interaction comes to be the first driving force in the stabilization of these anion–π interactions. The E\textsubscript{disp} values of ClO\textsubscript{3}\textsuperscript{−} (BrO\textsubscript{3}\textsuperscript{−}) complexes with coronene at the T and T-edge sites are −62.53 (−68.67) and −51.60 kJ/mol (−56.39 kJ/mol), respectively, which are more than two-fold larger compared with those of benzene, −25.49 (−26.55 kJ/mol). This dominant contribution of dispersion energy is accompanied by a considerable contribution of the induction force (E\textsubscript{ind} = −46.0 kJ/mol). This substantial increase in either E\textsubscript{disp} or E\textsubscript{ind} may be explained on the basis that the dispersion and induction interactions depend on the polarizabilities of the interacting partners, which, in turn, correlate with the...
flake size as well as the oxyanion size. Overall, one may predict that the anion-π interaction can be favorable even for the electron-rich benzene ring when the dispersion and induction energies are large enough to compensate for the repulsive electrostatic and exchange energies.

3.3. Non-covalent interaction (NCI) – reduced density gradient (RDG) analysis

The NCI analysis which is based on the reduced density gradient method (RDG) is very important in the characterization of weak interactions such as van der Waals interactions [62]. The RDG function is defined as:

\[
\text{RDG}(r) = \frac{1}{2} \left( \frac{\left[ \rho(r) \right]}{\rho(r)^{1/3}} \right)^2 \text{(2)}
\]

where \(\rho(r)\) is the electron density. By using Bader AIM theory, critical points where electron density is aggregated or depleted can be distinguished by the sign of the second largest eigenvalue of the Hessian matrix of electron density (\(\lambda_2\)). According to NCI analysis, weak interactions are found when \(\lambda_2 < 0\), strong attraction when \(\lambda_2 > 0\), and strong repulsion when \(\lambda_2 \sim 0\). Therefore, the sign of \(\lambda_2\) can give information about the nature of the interaction. Besides, the relative strength of the interaction correlate with the electron density \(\rho(r)\), for example: weak interactions have very small \(\rho\). Finally, defining a real space function \(\text{sign}(\lambda_2) \rho(r)\) and mapping it according to the RDG values gives us a live picture of the interaction type, figure 4.

Figure 4 (a) displays the NCI surface of the Down complexes of \(C_6H_6–XO_3^-\) and the most stable complexes of \(C_{24}H_{12}–XO_3^-\) (X = Cl, Br, I), while figure 4 (b) represents their scatter plots (RDG versus \(\text{sign}(\lambda_2)\rho\)). In the scatter plots, the regions where \(\text{sign}(\lambda_2) \rho(r)\) values are around 0.005 a.u correspond to dispersion interactions, while those of \(\text{sign}(\lambda_2) \rho(r) > 0.005\) a.u correspond to strong repulsion (e.g. steric effect) and \(\text{sign}(\lambda_2) \rho(r) < -0.005\) a.u values indicate strong attraction (e.g. hydrogen bonding). Careful inspection of Figure 4 reveals the absence of any hydrogen bonding in these types of interaction since there are no blue-colored surface in figure 4 (a) or blue spikes in figure 4 (b). Also, it verifies the significant role of dispersion interactions in oxyanion-π binding, the dispersion forces take place above the π-electron density of benzene and coronene (green color in figure 4 (a)). The plots show 2 green-colored spikes at the region of weak interactions. At last there are regions of red color that show areas of steric effect (repulsion) at the center of the rings due to the nonbonding overlap.

4. Conclusion

Based on this study, one may conclude the following: 1) The study demonstrates the presence of unexpected anion-π interactions between the oxyanions (\(\text{ClO}_3^–\), \(\text{BrO}_3^–\), and \(\text{IO}_3^–\)) and two of electron-rich π-systems (benzene and coronene). The origin of the binding in these complexes can be largely attributed to dispersion and induction effects, which, in turn, correlate with the increase in the polarizability of the interacting partners when going from \(\text{ClO}_3^–\) to \(\text{IO}_3^–\) and from benzene to coronene. 2) The increase in the adsorbent surface area when going from benzene to coronene introduces large unoccupied π-orbitals that results in a parallel increase of the binding strength due to the existence of charge transfer between the lone pairs of the anion oxygens and the π* orbitals of the coronene. This is why the Up orientations of the oxyanions on coronene are more stable than the Down orientations. 3) Moreover, it has been demonstrated that edge adsorption has the most stable binding energy which may be ascribed to the lowering of the repulsive electrostatic force when the anion is moved from the center to the edge. 4) Overall, it has been noticed that the increase in the polarizability and the electropositivity of the anions results in a parallel increase in the \(E_{ads}\) when going from \(\text{ClO}_3^–\) to \(\text{BrO}_3^–\) and to \(\text{IO}_3^–\). 5) These findings are hoped to help in further understanding of the different mechanisms in the binding of polyatomic anions with small or large π-systems and provide a potential application in the design of neutral anion receptors.
**Figure 4.** a) NCI surfaces (isovalue = 0.5 au) of C₆H₆ (1-3) and C₂₄H₁₂ (4-6) complexes at the M06-2X-D3/def2-TZVP level. The surfaces are colored on a blue-green-red scale according to values of $\text{sign}(\lambda_2)\rho$, ranging from -0.035 to 0.02 au. b) The corresponding scatter plots of reduced density gradient (RDG) versus the electron density $\rho$ multiplied by the sign of the second Hessian eigenvalue ($\lambda_2$) for each complex. (Cl: green; Br: dark red; I: purple).
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