On Halogen Bond Nature in OC[?][?][?]XY Systems from the Energy Decomposition Analysis Perspective

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Abstract

In this work have been presented the theoretical studies of the halogen bond nature based on six model complexes of O[?]C[?][?][?]X–Y type, where X and Y are halogen atoms. In these investigations, Local Molecular Orbital Energy Decomposition Analysis (LMOEDA) and Quantum Theory Atom in Molecules have been used as well as geometrical parameters and energy of intermolecular interaction and Molecular Electrostatic Potential (MESP). LMOEDA studies reveal a strong dependency on results on calculation methods. Some techniques have been given very consistence results with expectations; however, Grimme's dispersion corrections and some long-range separated functions in DFT do not work with used decomposition energy procedure. Electron density and Laplacian values confirm linear dependencies in connection to halogen bond energy than in the case of ΔE_{int}=f(RC[?][?][?]X). MEP calculations clearly indicate that for studied complexes the σ-hole theory is very useful to halogen bond description.

INTRODUCTION

The specific noncovalent intra- and intermolecular interactions as the hydrogen bond (HB), the charge transfer (CT) and the halogen bond designed also as XB in literature are today one of the main subjects of interests both of experimental and theoretical chemistry. There is nothing surprising in this, taking into account the fact that their role in general creating of matter, in the functioning of biological structures, and also usability in many current chemical technologies and nanotechnology is crucial.

The interaction through a halogen bond was the first time described in the nineteen century[1] but opposite to the hydrogen bond was very rarely mentioned in scientific papers. The main problem was with the interpretation of its formation mechanism and stability. The basic question was why negatively charged halogen atom can interact with electron-rich Lewis base? Only the sudden development of experimental and theoretical methods in chemistry and physics allowed shaping the different concepts that help today to understand much better many properties and meanings of XB in nature.

Actually, common theory answering the above question mostly was proposed by Politzer, Murray, and Clark.[2,3] It is so-called the σ-hole theory. This theoretical approach connects XB formation with the polarization of halogens in the molecule, its influence to charge distribution and finally determines the properties of the system. As the name itself already indicates the fundamental thing is here the σ-bond between atoms. Considering a simple exemplary D–X[?][?][?]Y scheme, where X is a halogen atom, Y is an electron-rich Lewis base (for example elements from 15 and 16 group of the periodic system and also anions of 17 group as F^-, Cl^-, Br^-, I^-)[4] or π-electrons. Whereas D may have got range from atoms like H, C, N, P and O to large inorganic or organic chemical groups containing very often heteroatoms and sometimes in a special case it may be also halogen atoms or groups.[5] Each of the halogens has on the valence shell seven electrons of which five of them on the p-orbitals. The most important (according to molecular orbital theory) electron that is necessary for σ-bond creation is located on p_z orbital. Formation of the single bond leads in these situations to the depopulation of p_z orbital, which is in the same line as the σ-bond. In this place, there is a region with electron deficiency designed as σ-hole. In other words, this positive charge on the X atom in a D–X monomer and the negative charge of Y interact electrostatically each other. This proposition of explanation of XB stability overthrows of the traditional way of reasoning, in which electron density is evenly distributed on X-atom.[6,7] The correctness of the σ-hole theory assumptions seem to be confirmed molecular electrostatic potential calculations (MEP).[8,9] In our own investigations, the MEP method also reveals a positive charge area in systems of X(1)-X(2) where both X are different halogen atoms connected by a single covalent bond. It will be more detailed discussed in the next parts of this paper.

An explanation based on this electrostatic approach has, unfortunately, like any theory, some weaknesses. Many theoretical methods give results dependent on adopted calculation models. Relative dispersion contribution is also discussed as well as concepts of charge transfer to these interactions types.[10]

The interaction energy is the main factor responsible for the build-up of supramolecular structures. In accordance with the postulates of quantum mechanics, the energy itself is observable. Referring to the chemical systems is the value of energy strictly related to atoms' positions and dependent on the electronic state of the complex. The most important thing is that the interaction energy can be minimized by its division into multiple terms. Such an approach focuses, in particular, on the individual components of interaction energy which the description from a physical point of view is less complicated.

Therefore, in this paper, it has been focused on the theoretical study of halogen bond not only from the MEP point of view but first of all from the perspective of an energy decomposition analysis and chemical quantum topology. The work in which energy partitioning was taken into account the first time is probably presented by London.[11] The two most important modern calculation techniques are SAPT (Symmetry-Adapted Perturbation Theory)[12] and LMOEDA (Localized Molecular Orbital Energy Decomposition Analysis).[13] LMOEDA has been conceived to solving many difficult chemical systems because it can be used in closed- and opened-shell complexes. Moreover, it includes many computational levels and takes into account the correction of the basis set superposition error. This procedure is today more and more widely used because of its not complicated to carry out and due to the easy accessibility to the software.[14-18] For these reasons, it was decided in this work to use LMOEDA as a tool for interaction energy decomposition. Quantum topological parameters of critical points each of the structures of monomers and complexes were studied using Quantum Theory of Atom in Molecules (QTAIM) methodology.[19]

From a chemical point of view in the area of interest was simple model complexes with pronounced interaction through halogen bonding. It was decided to take for research six four-atomic and closed-shell complexes about linear structure. Their general structure can be writing as O[?]C[?][?][?]X–Y, where X and Y are F, Cl, Br atoms arranged in the following order (X, Y)=F; (X, Y)=Cl; (X, Y)=Br; X=Br, Y=F; X=Br, Y=Cl; X=Cl, Y=F. Iodine atom was omitted due to the necessity to take into account effective core potentials (ECP) in calculations. Most of these complexes and monomers structures have been investigated experimentally (especially in spectroscopic terms) and some properties of them were also calculated using *ab initio*techniques.[20-26]

COMPUTATIONAL DETAILS

The whole project involved several stages of research: geometrical structures optimization of monomers and complexes, decomposition analysis of interaction energy in complexes, quantum topological studies every system and its component parts. All modelled systems have been investigated in a simulated gas phase state in a vacuum.

As for the geometrical structure optimization, the studies included several computational levels in Gaussian 16[27]and Molpro 2012.12.01[28] program packages (Molpro for coupled-cluster only). Among typical *ab initio* methods were used CCSD(T)[29-33] and MP2[34]. Whereas computations based on density functional theory (DFT) referred to the following exchange-correlation (XC) functional: B2GP-PLYP[35], B2PLYP[36], B3LYP[37,38], ωB97X[39] and M11[40]. Additionally, it was used also the dispersion correction of D2 and D3 developed by Grimme[41,42] for all of these functional except B2GP-PLYP (double hybrid functional) due to some technical troubles and except ωB97X where it was decided to the application only D2 correction implemented in ωB97X-D[43] XC functional. In turn, when it comes to basis sets have been applied aug-cc-pVDZ and aug-cc-pVTZ[44-46] in this work.

The interaction energy value each of the complex, ΔE_{int}, was generally obtained from the expression

$\Delta E_{\mathrm{int}} = E_{\mathrm{complex}} - (E_{\mathrm{OC}} + E_{\mathrm{XY}})$,(1)

where E_{OC} and E_{XY} are the total energies of monomers. It should be also noticed here that the basis set superposition errors (BSSE) in the case of systems optimization was removed in the procedure of the counterpoise method proposed by Boys and Bernardi[47]. Therefore the equation corrected energy can be written as the sum of equation (1) and mentioned amendment.

$\Delta E_{\mathrm{int}}^{\mathrm{CP}} = \Delta E_{\mathrm{int}} + \delta_{OC\bullet\bullet\bullet XY}^{\mathrm{BSSE}}$(2)

LMOEDA calculations were carried out using the GAMESS program package in version 2017.04.20-R1.[48] As a result of this decomposition procedure, the total interaction energy has been obtained as the sum

$\Delta\ E_{\mathrm{int}} = E_{\mathrm{ES}} + E_{\mathrm{EXC}} + E_{\mathrm{REP}} + E_{\mathrm{POL}} + E_{\mathrm{DISP}}$(3)

in which every component means electrostatic, exchange, repulsion, polarization and dispersion energy respectively. Electrostatic, polarization and dispersion energies are attractive, whereas the sum of the exchange and repulsion are repulsive.

QTAIM investigations have been especially focused on the analysis of Laplacian ([?]^{2}ρ(r)) of the electron charge density ρ(r), that refers to the (3, -1) critical points corresponding to bonds. All necessary here computations were performed using AIMAll 17.11.14 B program package.[49]

Electrostatic potentials were studied also in Gaussian 16 including cube files generation indispensable to the mapped of MEPs on the electron density surfaces.

The graphical part of this work was made in two programs: Chemcraft 1.8[50] and Gaussview 6[51].

RESULTS AND DISCUSSION

Geometrical structure parameters of studied systems

Figure 1 show in a schematic way investigated structures of modelled complexes obtained using one of the presented above calculations methods. All geometrical structures are of course linear. Each of the systems and monomers achieved a minimum on the potential energy surface during the optimization procedure what was confirmed by obtained frequencies values. There were no imaginary frequencies designed in Gaussian and Molpro as a negative value.

The most important structural parameters of this work are intermolecular interaction distances as one of the main properties responsible for complex stability and its reactivity. The calculated carbon-halogen interaction distances values have been presented in Table 1. Four of six studied here systems were also the subject of experimental investigation. Those studies focused, first of all, on the spectroscopic properties and charge contribution inside complexes appearing in their gas phase. Obtained in experiments values of intermolecular distances referring to the interesting systems have been also collected in Table 1.

The most predictable changes of the values showed here OC[?][?][?]BrF and OC[?][?][?]ClF. In the first of them, the interaction distance is the shortest in every used computational technique and basis set and in the second place in this regard is OC[?][?][?]ClF. The next is the OC[?][?][?]F_2 and OC[?][?][?]BrCl. Unfortunately, in the case of OC[?][?][?]F_2 occur some disproportions. It can be seen on the level ωB97X-D of theory where the C[?][?][?]F distance is the longest among all complexes and this result, including aug-cc-pVDZ basis set, is equal 3.407Å and for aug-cc-pVTZ 3.472 Å. It is [?] 0.5 A longer than the optimized structure comes from the same exchange-correlation functional without dispersion correction. M11 functional in a combination of aug-cc-pVTZ has been given in the case of OC[?][?][?]F_2complex about 0.186 A longer interaction distance than in OC[?][?][?]BrCl. For the double zeta basis set these discrepancies do not occur. If the last two complexes (OC[?][?][?]Br_2, OC[?][?][?]Cl_2) will be considered in the order of increasing interaction distances the situation from a calculation point of view is not especially clear. Experimental data distinctly indicate that carbon-halogen interaction is longer about 0.082 A in OC[?][?][?]Cl_2. Taking into account the results obtained by using the aug-cc-pVDZ basis set the same quality dependencies as in the experiment are preserved in case of using double hybrid functionals (excluding B2GP-PLYP) (also with empirical dispersion D2 and D3 corrections), B3LYP, ωB97X, and M11. Whereas the same results for the aug-cc-pVTZ basis set reveal in addition that B2PLYP-D2 and B2PLYP-D3 also do not keep the direction consistent with the experiment. Summarizing the above, the following relationship may be written for the C[?][?][?]X distance from the shortest to the longest:

$$OC\bullet\bullet\bullet \mathrm{BrF} < OC\bullet\bullet\bullet ClF < OC\bullet\bullet\bullet F_2 \text{ (except } \omega B97XD \textit{ and } M11) <$$

$$< OC\bullet\bullet\bullet BrCl < OC\bullet\bullet\bullet \mathrm{Br}_2 < OC\bullet\bullet\bullet \mathrm{Cl}_2 (\textit{depends on the method}). \quad (4)$$

Intermolecular distance considerations, in relation to different computational levels within each of the basis sets, have been shown there is no simple correlation.

Table 2 illustrates the changes in bond length between halogen atoms (X–Y) after complex creation. The values there are given (in angstroms) as the result of the expression

$$\Delta R_{XY} = R_{XY}^{\text{complex}} - R_{XY}^{\text{monomer}}. \quad (5)$$

The O[?]C distance was not included in Table 2 because the biggest difference of it between complex and monomer not exceeded ±0.004 Å. Skipped also results for aug-cc-pVDZ. It was noted that the equation (5) has been given practically the same values for both basis set. The differences between aug-cc-pVDZ and aug-cc-pVTZ for the same complexes and techniques were about ±0.004 Å for X–Y bond lengths and maximum ±0.001 Å in case of O[?]C.

Analysis of the mentioned table draws attention to two things. Firstly all the changes are positive. It means that all bonds have been slightly elongated when the complexes were formed. The highest values are observed for Br–F, whereas the lowest for F–F. As for used calculations techniques, the most changes of halogen-halogen bond lengths of investigated systems in relation to the isolated dihalogen monomers are visible for B3LYP and its modification after adding dispersion correction both of D2 and D3. For example, $R_{\mathrm{Br-F}}$ for these mentioned methods is equal approximately 0.05 A and for CCSD(T), MP2 and M11 0.015 A, 0.022 A and 0.012 A respectively, what together with ωB97X (0.017 Å) gives the smallest changes here. Such dependence repeats more or less for all complexes.

At the end of this part, it should be stated that the largest interacting distances C[?][?][?]X usually correspond to those molecular systems where the dipole moment values of electron donors are the smallest. It is visible here in the case of the BrF group that shortens halogen bond length the most and Br_2 or Cl_2 act inversely. Interatomic distance is, therefore, one of several parameters helpful in understanding the nature of XB. Whereas for investigated model monomers the results collected in Table 2 are very small which leads to the conclusion that geometrical changes in monomers groups are rather negligible and the investigated specific interaction creation has no influence on the physicochemical properties of O[?]C and X–Y groups.

Interaction energy and its decomposition

It was already above mentioned that the LMOEDA procedure gives five energy terms, where their sum is corresponding to the interaction energy. The electrostatic component refers to the repulsion between electrons and the attraction between electrons and atomic nucleus as well as the nucleus-nucleus repulsion. In contrast to the SAPT, LMOEDA treats exchange and repulsion energy contributions separately. In fact, both energy types are strictly related to the Pauli exclusion principle. Polarization energy change includes so-called orbital relaxation i.e. orbital modifications during and after complex creation. The last term is the London dispersion energy, which is always attractive and is associated with electron correlation.

In this work, all interaction energies have been included BSSE correction. All energy values coming from LMOEDA calculations are collected in Table S1 in support information. This table has been also enriched by interaction energies values designed as $\Delta E_{\rm int}$(opt). Letters ,,opt" mean that $\Delta E_{\rm int}$ values do not come from LMOEDA procedure, but they are obtained based on the optimized structures of complexes and monomers and their total energies calculated in Gaussian and Molpro program packages according to the formula (1) and (2). It is very important to compare different methods and draw appropriate conclusions as to their correctness.

In Figure 2 there are presented bare graphs that show interaction energy components (in kcal/mol) for used here calculations techniques. The data refer to the aug-cc-pVTZ basis set only because the results for aug-cc-pVDZ and aug-cc-pVTZ are quite like each other especially in terms of quality. The mentioned Table S1 includes both basis sets. However, Figure 2 does not consider DFT methods with dispersion correction. Exchange-correlation functionals with D2 and D3 have been considered separately due to technical and computational reasons. In every case, it was added for comparison (apart from individual component energies) the values of total interaction energies, $\Delta E_{\rm int}$, obtained also from the decomposition energy method. Bar plots illustrate also (yellow bar) the sum of exchange and repulsion energy for every complex. Exchange energy is rather stabilizing energy but repulsion energy on the contrary. These two quantities act in opposite directions however they behave according to a similar scheme. Hence it was decided to group them into a single term called EX+REP.

From the first five graphs, (a)÷(e), (see Figure 2) some conclusions can be drawn. First of all, it is that the biggest absolute energy values occur always for the OC[?][?][?]BrF complex independently from the used calculation level. It refers to each individual energy type and to interaction energy as well. Outstanding this system from others can be explained through interatomic interaction distance analysis. As it appears from the already discussed Table 1 the shortest XB is just for OC[?][?][?]BrF. The consequence of it should be the lowest value of interaction energy. It was confirmed both for $\Delta E_{\rm int}$obtained from LMOEDA and in the calculation of $\Delta E_{\rm int}$(opt). The next shortest C[?][?][?]X distance is in OC[?][?][?]ClF. It was also reflected in mentioned energies values and in total interaction energy. Graphs from (a) to (e) presented in Figure 2 confirm similar dependencies for systems in relation to different used here methods although DFT functionals seem to have got tend to overestimate components and interaction energies values. The biggest energy scale scattering has been given B2PLYP and B3LYP techniques (from about -40 to almost 100 [kcal/mol]).

Arousing the most doubts are here the calculations at the ωB97X and M11 level of theory. LMOEDA does not work especially well with these DFT functionals. Final results in the interaction energies form seem to be reliable but component energies are irrational. As indicated in Figure 2 and Table S1 the values of electrostatic (ES) and polarization (POL) energies are huge. In addition, ES is positive. As it is shown in the attached table even exchange energy for ωB97X is positive in the case of OC[?][?][?]Cl_2 and OC[?][?][?]F_2. The conclusion from this is some long-range separated functionals should be excluded from energy decomposition computations of used here procedure.

The next question is how the Grimme's dispersion correction does work with implemented in GAMESS algorithms? The answer has been illustrated by means of Figure 3 and Table 3. Figure 3 represents linear plots of $\Delta E_{\rm int}$ and $\Delta E_{\rm int}$(opt) (in kcal/mol) values calculated for every six complexes in the aug-cc-pVTZ basis set. The chart (a) refers to the double-hybrid B2PLYP-DN XC functionals, where N=2, 3. Whereas B2PLYP (B2PLYP-DN str.) means that the geometrical structure of complexes was optimized at the B2PLYP-DN level and LMOEDA was carried out without proper dispersion correction. The symbol ,,opt", as earlier was described, includes interaction energy calculated directly from Gaussian or Molpro (CCSD(T)) program packages but with taking into account BSSE. The investigations omitted B2GP-PLYP-DN functional because both in Gaussian and GAMESS dispersion is bad implemented for it. As a result, it was obtained identical values for B2PLYP-DN and B2GP-PLYP-DN. In turn, the charts (b) and (c) include B3LYP and ωB97X respectively and their enriched about DN versions. In Table 3 there are additionally collected $\Delta E_{\rm int}$ and $\Delta E_{\rm int}$(opt) values of complexes for B3LYP and B3LYP-D3 only, to better visualize the changes after the used of dispersion (for both basis sets).

The analysis of Figure 3 should be noticing some similar relationships for each of the three presented methods. Firstly, interaction energies obtained by using pure functionals (without dispersion correction) both in

LMOEDA and in standard approach are very similar. The lines almost overlap themselves. It is evidence that the results coming from three different programs can be compared to each other and computations are reliable. Secondly, energy decomposition procedure when dispersion was not included in DFT functionals but the geometrical structures of complexes were earlier optimized with added empirical dispersion correction gives also very similar ΔE_{int} values as in case of the structures obtained without DN correction despite the small differences in geometrical parameters of studied systems. For example, curves B2PLYP, B2PLYP (B2PLYP-D2 str.), B2PLYP (B2PLYP-D2 str.)-opt, (B2PLYP-D3 str.) and (B2PLYP-D3 str.)-opt are almost identical. On the other hand, however performances of LMOEDA calculations taking into account dispersion correction have been given completely different and senseless values of interaction energies. It is especially visible for B3LYP-DN and ωB97X-DN techniques. Table 3 shows that ΔE_{int} in relation to ΔE_{int}-opt is not only incomparable in any way but for OC[?][?][?]Cl_2 and OC[?][?][?]F_2 is also positive (for B3LYP-D3). The presented table in support information to this publication contains more such irregularities. Moreover, Su *et al* .[56]unambiguously confirmed that the current LMOEDA version does not work properly with functionals containing dispersion correction and the functions corresponding for long-range description.

To better understand the meaning of each kind of component energy in halogen bond creation of investigated systems Figure 4 was depicted. The bar plots here contain energetic data in percentage terms in relation to the concrete complex. The values, as in earlier figures, include the aug-cc-pVTZ basis set only. It was inserted the results referring to the following calculation methods: typical *ab initio* CCSD(T) and MP2 techniques, double hybrid B2PLYP functional and the most known hybrid DFT functional i.e. B3LYP. As it was revealed above the ωB97X, M11 and all dispersion enriched functionals had to be skipped.

As one can expect, the contributions of individual energies in the charts indicate clearly that both CCSD(T) and MP2 results are quite closed to each other especially in terms of quality. Electrostatics and dispersion play here the most important role in the stabilizing of the complexes structure, however in the case of OC[?][?][?]F_2 the dispersion effects increase significantly in comparison to the electrostatic forces. Whereas for OC[?][?][?]BrF and OC[?][?][?]ClF dispersion gets lower for the benefit of polarization energy. An energy decomposition result obtained by using density functional theory reveals a bit different dependence. As it was showed on the (c) and (d) plots the main factor responsible for the systems' indestructibility is electrostatic and polarization energies. In the case of calculations at the B2PLYP level of theory, the dispersion and polarization contribution are almost the same for OC[?][?][?]F_2, whereas electrostatic and polarization energies are comparable in OC[?][?][?]BrF and OC[?][?][?]ClF structures. Somewhat closer to the CCSD(T) and MP2 plots are the bars presented in (d) diagram. From all negative values in OC[?][?][?]F_2 the DISP is the most significant as in *ab initio* and in the rest of the systems, the tendencies are similar. In the end, it must be said that the greater halogen bond energy, the less participation of dispersion energy in it and the bigger the meaning of polarization.

QTAIM and ESP analysis

The last step of the research was to better understand the dependencies governing the electron density and charge distribution in investigated systems and their influence on the XB formation.

Quantum Theory Atom in Molecules (QTAIM) allowed finding and analysis all critical points referring to the structure of each complex and monomer. In this work, the main interesting objects are these corresponding to create of bonds and intermolecular interaction. They are so-called Bond Critical Points (BCPs) represented by saddle point (3, -1) taking into account the direction of electron density changes.

The result data coming from calculations carried out in the AIMAll program package had been revealed seven critical points, two of which included bonds and one refers to intermolecular C[?][?][?]X interaction. Figure 5 illustrates the exemplary deployment of BCPs based on the OC[?][?][?]BrF structure. Coordinates of these points are almost the same in the case of each complex. Notice the BCP corresponding O[?]C bond is displaced to the oxygen direction. The other two of these points are rather located symmetrically.

Considerations have been included here following five parameters and the relationships between each other:

interatomic distances and bond lengths; total interaction energies (ΔE_{int} and ΔE_{int}-opt); electron density values (ρ(r)) and Laplacian of the electron density ([?]^{2}ρ(r)). Similarly as in case of decomposition energy significant part of results has been placed in support information in table form designed as Table S2. This table contains total interaction energies and Laplacian of the electron density values for every used here calculation method in both basis sets. It needs to be highlighted that the AIMAll program package does not include triple excitations in the coupled-cluster method. Thus, it was used CCSD technique for the structures optimized at CCSD(T) level of theory. [?]^{2}ρ(r) in the mentioned table refers to the BCP localized between two monomers, O[?]C and X–Y, that corresponds to halogen bond. [?]^{2}ρ(r) values play a significant role in studies of the properties of chemical bonds because they specify where the electron density is the most concentrated. This quantity is directly related to potential energy (V(r)), and the density of kinetic energy (G(r)). The equation connecting these parameters to each other can be written as

$\frac{\nabla^2(\rho)}{4} = 2G\left(r\right) + V\left(r\right)$. (6) It should be pay attention also for the sign of [?]^{2}ρ(r). The negative values of [?]^{2}ρ(r) mean that V(r) is in local excess. In the opposite situation, the charge is more depleted and the G(r) is a dominant factor. As can be seen in the attached table all results for Laplacian are positive. The papers[57,58] proves, that [?]^{2}ρ(r)>0 occurs in the case of closed-shell interactions.

Table 4 is enriched (except ΔE_{int} and [?]^{2}ρ(r)) with additional already mentioned parameters: distances, ρ(r) and [?]ρ(r). It was focused here on a detailed analysis of the results obtained at two calculation levels: CCSD and B3LYP. Considerations of Table 4 reveals that the O[?]C bond lengths and topological parameters of BCP are very similar in every complex calculated by using the same method and basis set. Density and Laplacian values are here positive, and it is typical for covalent polar bonds.[59] What is interesting, however, the differences between basis sets are very significant especially for [?]^{2}ρ(r). Notice that [?]^{2}ρ(r) of O[?]C is more than two times higher in the case of aug-cc-pVDZ at the CCSD level and over and above three times for the B3LYP method in comparison to aug-cc-pVTZ results. Whereas the Laplacian values for the X–Y bond type are very low, and they have various signs (positive or negative), that suggests the different character of X–Y bond. For example, the shortest distance here is in the case of F–F in OC[?][?][?]F_2 and the [?]^{2}ρ(r) gives the highest numbers. However, generally, there are no unambiguous dependences between bond lengths and Laplacian values. The Cl–F bond length in OC[?][?][?]ClF is the second shortest distance of X–Y among all studied systems but for presented two calculations methods in the aug-cc-pVTZ basis set have the lowest (negative) values of [?]^{2}ρ(r). This may suggest more shared shell interaction what practically means the stronger covalent bond character. It is worth to pay attention that in the case of a halogen-halogen bond, there occur a bit more disproportionate differences in values and signs of Laplacian (depending on the adopted computational method and basis set) than for O[?]C bond and halogen bond.

Halogen bond geometrical, energetic and topological parameters were presented not only in Table 4 and in the enclosed Table S2, but the data was also depictured in Figures 6-8. Figure 6 contains four plots illustrating interaction energy, halogen bond length, electron density and Laplacian as a function of complex type. It can be seen immediately some dependencies between proper curves. Plots (c) and (d) have almost identical shapes with this exception, that in the case of [?]^{2}ρ(r), the values are about two times higher than for ρ(r). In turn, on the plots (a) and (b) the most significant differences are noticeable for the OC[?][?][?]F_2 system, where for the weakest interaction the range of XB is shorter than for stronger halogen bonds in OC[?][?][?]Br_2, OC[?][?][?]Cl_2 and in OC[?][?][?]BrCl. It is also visible, that the B3LYP technique had been given less dispersion of results between used basis sets, particularly for the cases of OC[?][?][?]BrF and OC[?][?][?]ClF systems presented on the plots (a)÷(c). Summarizing Figure 6, with the assumption of omission of OC[?][?][?]F_2 complex, the general tendency is that the shorter XB the greater the value of electron density and Laplacian. It seems the correlations between halogen bond power and structural or topological parameters should be easier to find because investigated systems have the same Lewis base and different Lewis acids. Plots in Figure 7 indicate to a lesser or greater extent on certain dependencies. Plot (a) illustrates $\Delta E_{\text{int}}=f(R_{C[?][?][?]X})$ and the slope of the straight lines is positive in comparison to other plots that are coincident with information from the previous figure. Nevertheless, the correlation coefficients especially these referring to the CCSD level are very low (R^2[?]0.32 or R^2[?]0.54). The situation on the plot (b) looks a little better. Laplacian values in relation to the XB length had been given determinant coefficients equal to R^2[?]0.64 or R^2[?]0.79 for CCSD/aug-cc-pVDZ and CCSD/aug-cc-pVTZ respectively. In the case of the DFT method, the fitting is very well (R^2>9). Much better functions for the description of XB strength can be obtained by the replacement $R_{C[?][?][?]X}$ by $\rho(r)$ or by $[?]^2\rho(r)$ and it was presented on the plots (c) and (d) in Figure 7. The linear dependence of interaction energy relative to one of the mentioned topological parameters is here greater than 0.9. Hence the conclusion is that the parameters obtained by using QTAIM methodology give much more predictable results in studies of XB strength than in the case of traditional geometrical data.

The molecular electrostatic potential distribution has been shown in the form of electrostatic potential plot in Figure 8 and was generated for the three monomers (OC, Br_2, ClF) and two complexes (OC[?][?][?] Br_2 and OC[?][?][?]ClF). Presented MEP calculations were carried out at the B3LYP/aug-cc-pVTZ level of theory. From the pictures can be concluded that the σ-hole is observed for Br–Br and Cl–F, but in the first case, the positive charge is at the cusp point from both sides (on every Br atom). Whereas the second monomer has a positive charge, that is focused at the peak of the chlorine atom. The most intensive blue colour means the most positive charge with the values of about 0.03 a.u. It is also clear that the electron-rich area on the carbon and oxygen atom can be a very good candidate for the creation of directional interaction. The pictures (c) and (d) refer to the formed complexes where changes of MEP are not drastic in comparison to monomers.

CONCLUSIONS

The main aim of this paper was to analysis six complexes with linear interaction through halogen bond from the point of view of their interaction energy and influences this energy and every one of its components for the halogen bond formation and strength. Investigated complexes are not only theoretical systems but they are also synthesized fully, and they were an object of few experimental studies.

In the first place, it was tried to find the dependencies between the lengths of proper bonds before and after XB creation. As was shown the changes for O[?]C were negligibly small. Also, in the case of XY, the bond length changes between monomers and complexes were very small although all XY bonds lengthened itself after the creation of complexes, what was the most visible for the B3LYP method. In addition, there were no significant differences between used basis sets. In turn, for carbon-halogen interaction distance, finding more precise correlations was not so easy. The shorter XB was noted for the OC[?][?][?]BrF complex and then for the OC[?][?][?]ClF in every used computational technique. Other systems have less predictable dependencies much closer related to the adopted method of studies.

LMOEDA generally had been given reliable results except for two things. Firstly, the using ωB97X and M11 leads to irrational enormous values of electrostatics and polarization energies and the second thing is completely bad working this procedure with exchange-correlation functionals enriched of Grimme's dispersion corrections, and particularly with B3LYP-DN and ωB97X-D, where the total interaction energy values for the OC[?][?][?]F_2 was unfortunately positive (in the case of B3LYP-D3 it was observed positive energy for OC[?][?][?]Cl_2 as well). Additionally, B2GP-PLYP is in the opinion of authors bad implemented in Gaussian as well as in LMOEDA algorithms in GAMESS because the results were identical as in the case of B2PLYP, both at geometrical properties level obtained in the optimization process and for energy decomposition. The component energy playing the main role in the stabilizing of the complexes structure was different and depending on the method. Generally, it can be said that for *ab-initio* techniques they were electrostatics and dispersion energies. Whereas in the case of DFT theory dispersion decreased in relation to the polarization energy.

QTAIM theory was used for finding and description of bond critical points (3, -1) in investigated modelled complexes. For every system are three such points. Two of them correspond to the covalent bonds between atoms in monomers parts and the third is localized between C and X atom and refers to noncovalent interaction, this is halogen bond. The analysis of the results indicates that for this BCPs the values of $\rho(r)$ and $[?]^2\rho(r)$ are all positive what means that G(r) in equation (6) plays a dominant role. It is visible to closed-shell interaction. It should be noted here that the topological parameters are better for comparison of the strength of halogen bonds because dependences of interaction energies in relation to one of the mentioned above parameters are more linear.

In the end, molecular electrostatic potential confirmed the creation of a positive charge region on halogen atoms called the σ-hole and on the other hand the accumulation of negative charge on carbon and oxygen atom. As it is commonly known plus and minus charge can form attractive forces between each other what leads to the stabilization of such complexes as presented here.

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CONFLICTS OF INTEREST

Authors declare no conflicts.

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LIST OF FIGURES

Figure 1. Schematic presentation of model systems including intermolecular halogen bonding constituting the subject of the studies.

Figure 2. Contributions of individual energy components in total interaction energy as LMOEDA result. ΔE_{int} was also presented on charts for comparison. The charts included calculations carried out in the aug-cc-pvTZ basis set.

Figure 3. Plots illustrating differences in ΔE_{int} for used exchange-correlation functionals, with and without empirical dispersion correction of Grimme. The data include each complex (aug-cc-pVTZ basis set). The three charts present results obtained at the (a) B2PLYP, (b) B3LYP and (c) ωB97X level of theory respectively, as the basic XC functionals.

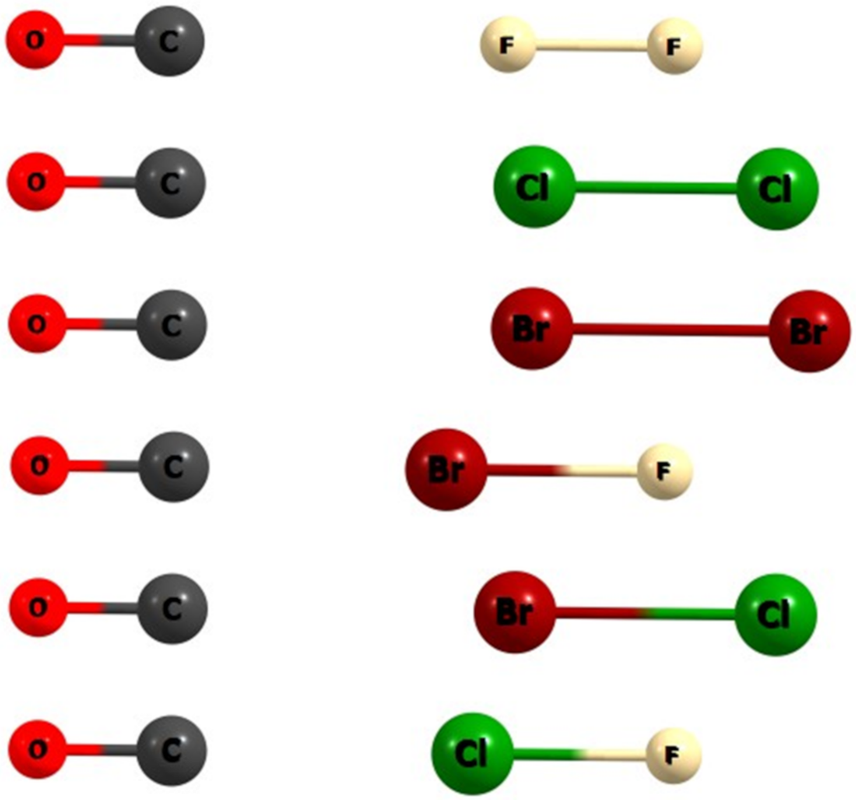
Figure 4. Stacked bars plot of percentages shares of component energies including four selected methods: (a) CCSD(T)/aug-cc-pVTZ, (b) MP2/aug-cc-pVTZ, (c) B2PLYP/aug-cc-pVTZ and (d) B3LYP/aug-cc-pVTZ.

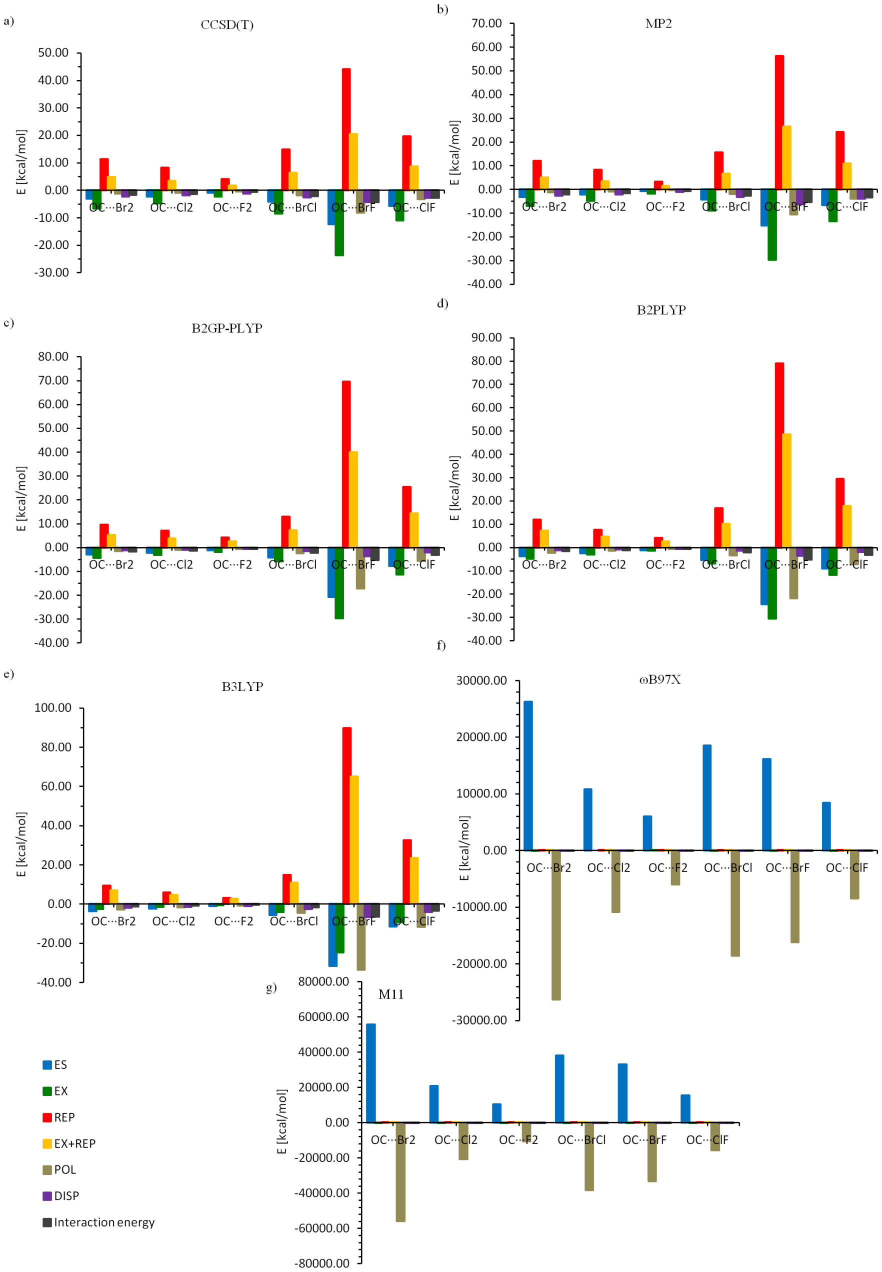
Figure 5. One of the complex structures o(OC[?][?][?]BrF) as an example of critical bonding points (3, -1) deployment. Results obtained in the AIMAll program package at the MP2 level of theory using the aug-cc-pVDZ basis set.

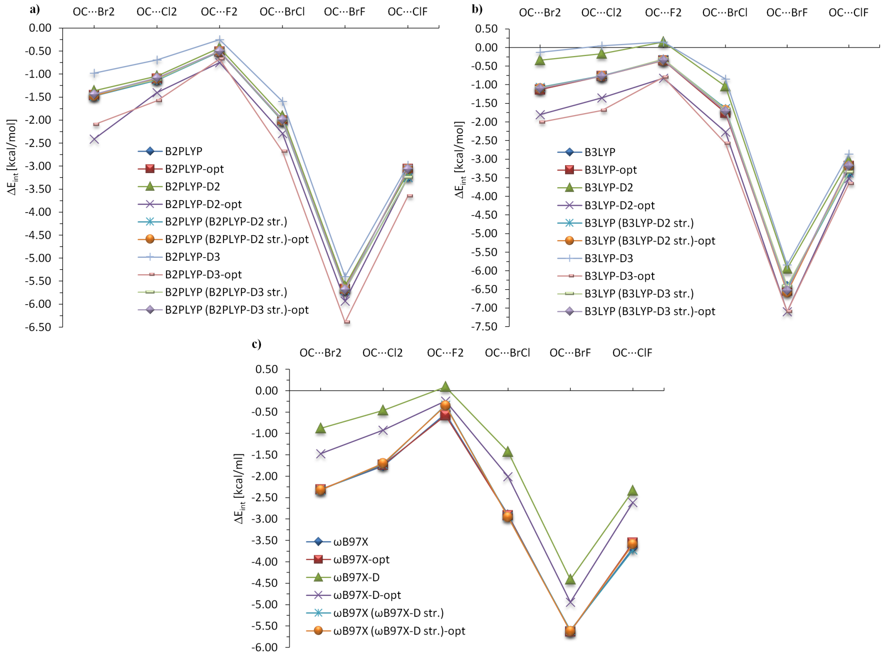
Figure 6. Plots showing (a) ΔE_{int}[kcal/mol], (b) C[?][?][?]X interaction distance [Å], (c) electron density [a.u.], (d) Laplacian of density [a.u.] for every complex type. It has been selected two computational methods for comparison: CCSD and B3LYP in both basis sets. All data here refers to the intermolecular BCP.

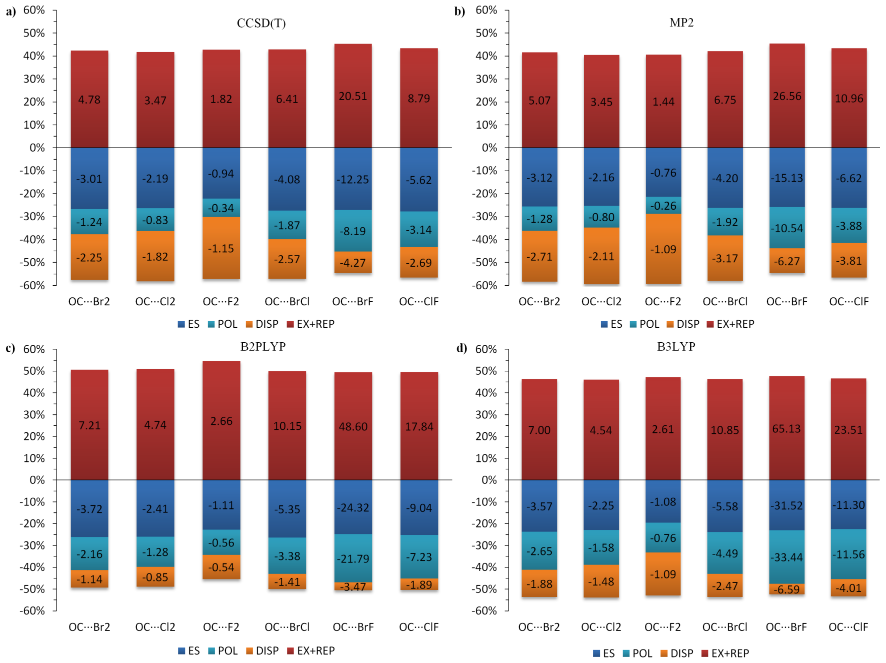
Figure 7. Correlations between interaction energies and (a) XB binding distances, (c) electron density, (d) Laplacian of density. Whereas the second plot (b) indicates Laplacian of density as a function of XB distance.

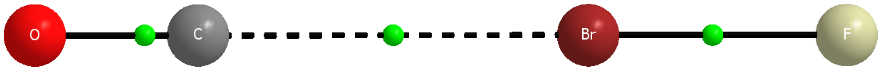
Figure 8. Exemplary electrostatic potential mapped on the surface of molecular electron density at the B3LYP/aug-cc-pVTZ level of theory for (a) OC, (b) Br_2 and ClF, (c) OC[?][?][?]Br_2, (d) OC[?][?][?]ClF.

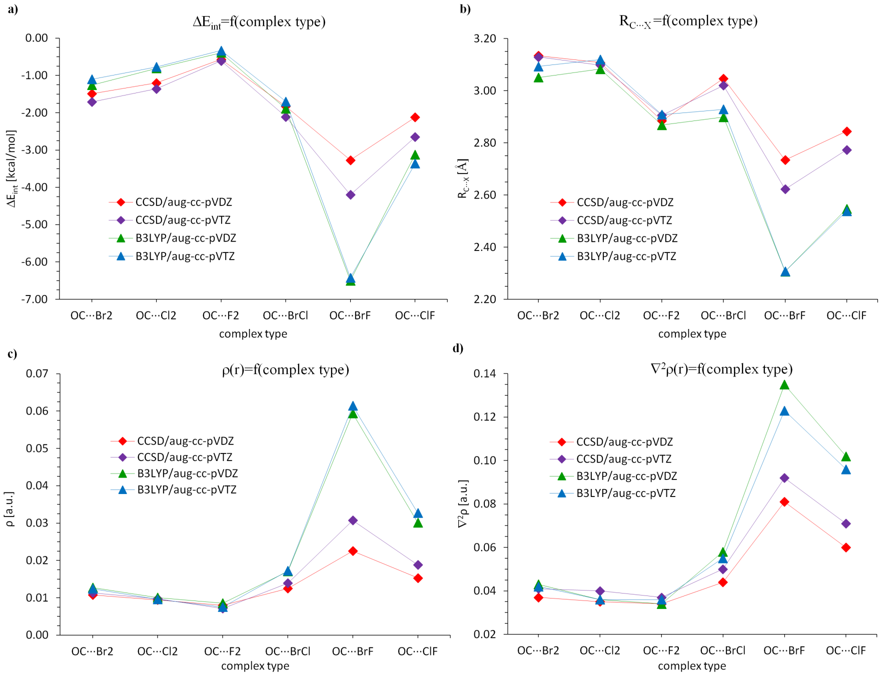

O
C
F
F
O
C
Cl
Cl
O
C
Br
Br
O
C
Br
F
O
C
Br
Cl
O
C
Cl
F

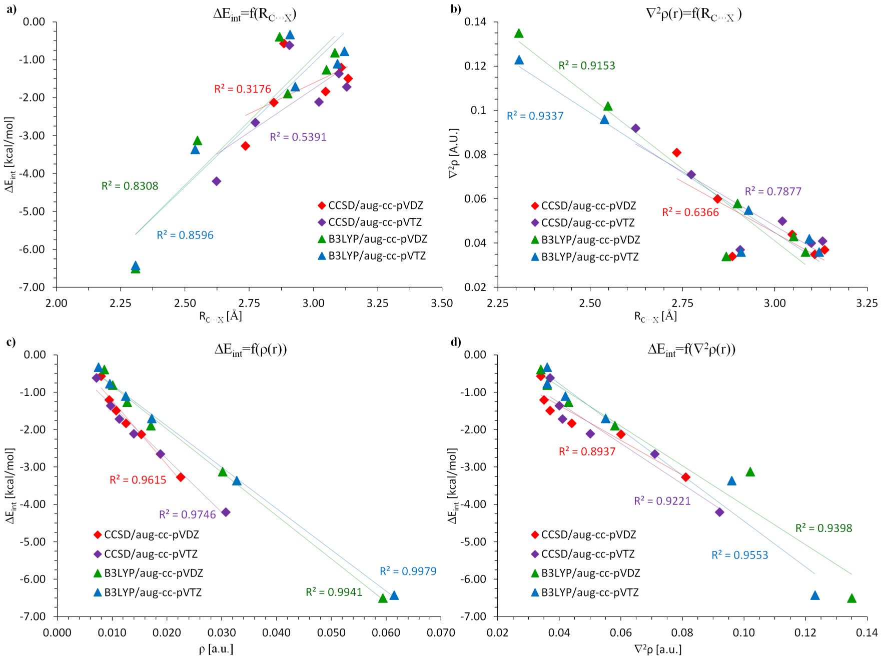

a)
CCSD(T)
E [kcal/mol]
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
OC···Br2
OC···Cl2
OC···F2
OC···BrCl
OC···BrF
OC···ClF
b)
MP2
70.00
60.00
50.00
40.00
-40.00
c)
B2GP-PLYP
80.00
d)
B2PLYP
90.00
e)
B3LYP
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
-40.00
f)
ωB97X
30000.00
20000.00
10000.00
0.00
-10000.00
-20000.00
-30000.00
g)
M11
80000.00
60000.00
40000.00
20000.00
0.00
-20000.00
-40000.00
-60000.00
-80000.00
ES
EX
REP
EX+REP
POL
DISP
Interaction energy

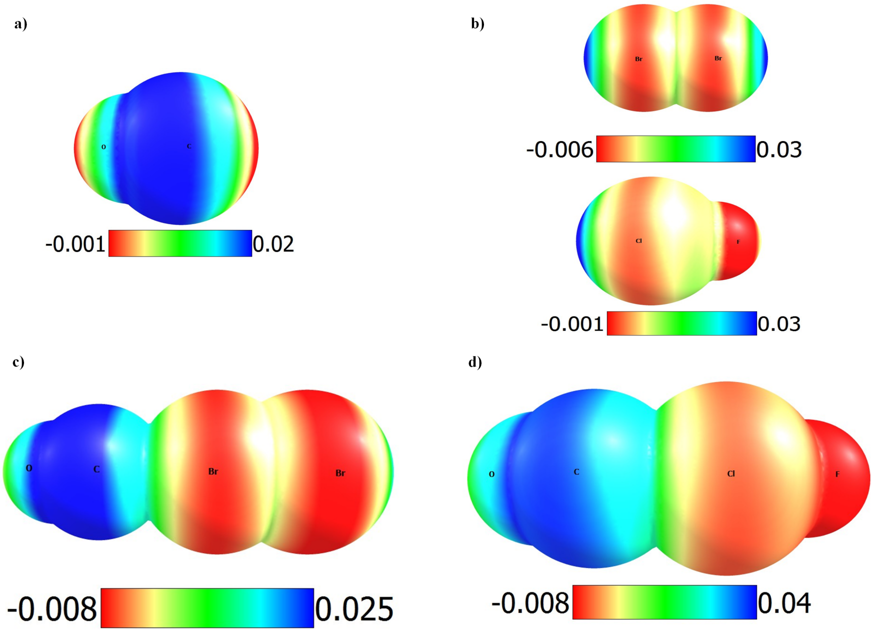

a)
OC···Br2
OC···Cl2
OC···F2
OC···BrCl
OC···BrF
OC···ClF
ΔE_int [kcal/mol]
B2PLYP
B2PLYP-opt
B2PLYP-D2
B2PLYP-D2-opt
B2PLYP (B2PLYP-D2 str.)
B2PLYP (B2PLYP-D2 str.)-opt
B2PLYP-D3
B2PLYP-D3-opt
B2PLYP (B2PLYP-D3 str.)
B2PLYP (B2PLYP-D3 str.)-opt
b)
ΔE_int [kcal/mol]
B3LYP
B3LYP-opt
B3LYP-D2
B3LYP-D2-opt
B3LYP (B3LYP-D2 str.)
B3LYP (B3LYP-D2 str.)-opt
B3LYP-D3
B3LYP-D3-opt
B3LYP (B3LYP-D3 str.)
B3LYP (B3LYP-D3 str.)-opt
c)
ΔE_int [kcal/ml]
ωB97X
ωB97X-opt
ωB97X-D
ωB97X-D-opt
ωB97X (ωB97X-D str.)
ωB97X (ωB97X-D str.)-opt


a) CCSD(T)
4.78 3.47 1.82 6.41 20.51 8.79
-3.01 -2.19 -0.94 -4.08 -12.25 -5.62
-1.24 -0.83 -0.34 -1.87 -8.19 -3.14
-2.25 -1.82 -1.15 -2.57 -4.27 -2.69
b) MP2
5.07 3.45 1.44 6.75 26.56 10.96
-3.12 -2.16 -0.76 -4.20 -15.13 -6.62
-1.28 -0.80 -0.26 -1.92 -10.54 -3.88
-2.71 -2.11 -1.09 -3.17 -6.27 -3.81
c) B2PLYP
7.21 4.74 2.66 10.15 48.60 17.84
-3.72 -2.41 -1.11 -5.35 -24.32 -9.04
-2.16 -1.28 -0.56 -3.38 -21.79 -7.23
-1.14 -0.85 -0.54 -1.41 -3.47 -1.89
d) B3LYP
7.00 4.54 2.61 10.85 65.13 23.51
-3.57 -2.25 -1.08 -5.58 -31.52 -11.30
-2.65 -1.58 -0.76 -4.49 -33.44 -11.56
-1.88 -1.48 -1.09 -2.47 -6.59 -4.01
OC···Br2 OC···Cl2 OC···F2 OC···BrCl OC···BrF OC···ClF
ES POL DISP EX+REP


O
C
Br
F


a)
ΔE_int=f(complex type)
ΔE_int [kcal/mol]
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
-6.00
-7.00
complex type
b)
R_C···X=f(complex type)
R_C···X [Å]
3.20
3.00
2.80
2.60
2.40
2.20
c)
ρ(r)=f(complex type)
ρ [a.u.]
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
d)
∇²ρ(r)=f(complex type)
∇²ρ [a.u.]
0.14
0.12
0.10
0.08
0.06
0.04
0.02
OC···Br2
OC···Cl2
OC···F2
OC···BrCl
OC···BrF
OC···ClF
CCSD/aug-cc-pVDZ
CCSD/aug-cc-pVTZ
B3LYP/aug-cc-pVDZ
B3LYP/aug-cc-pVTZ


a)
ΔE_int=f(R_C···X)
ΔE_int [kcal/mol]
R_C···X [Å]
2.00
2.25
2.50
2.75
3.00
3.25
3.50
R² = 0.3176
R² = 0.5391
R² = 0.8308
R² = 0.8596
b)
∇²ρ(r)=f(R_C···X)
∇²ρ [A.U.]
R² = 0.9153
R² = 0.9337
R² = 0.7877
R² = 0.6366
c)
ΔE_int=f(ρ(r))
ρ [a.u.]
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.070
R² = 0.9615
R² = 0.9746
R² = 0.9979
R² = 0.9941
d)
ΔE_int=f(∇²ρ(r))
∇²ρ [a.u.]
0.02
0.04
0.06
0.08
0.10
0.12
0.14
R² = 0.8937
R² = 0.9221
R² = 0.9398
R² = 0.9553
CCSD/aug-cc-pVDZ
CCSD/aug-cc-pVTZ
B3LYP/aug-cc-pVDZ
B3LYP/aug-cc-pVTZ


a)
O
C
-0.001
0.02
b)
Br
Br
-0.006
0.03
Cl
F
-0.001
0.03
c)
O
C
Br
Br
-0.008
0.025
d)
O
C
Cl
F
-0.008
0.04