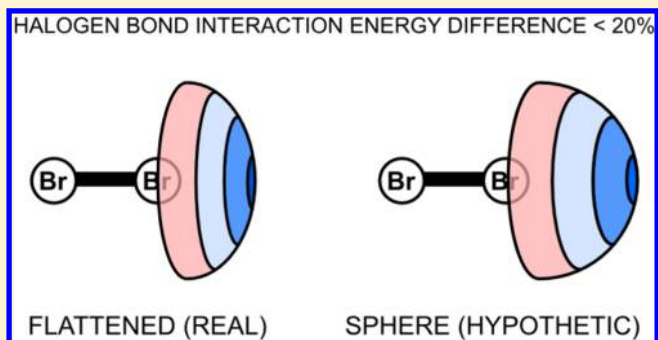


Polar Flattening and the Strength of Halogen Bonding

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ABSTRACT: The effect of polar flattening on the stability of 32 halogen-bonded complexes was investigated by utilizing CCSD(T)/CBS, DFT, and DFT-SAPT/CBS methods. It is shown that the value of polar flattening increases with the decreasing value of studied isodensity. For the complexes investigated, the polar flattening based on the isodensity of 0.001 au reaches 0.2–0.3 Å and 10–15% in absolute and relative values, respectively. These geometrical changes induce differences in the stabilization energy up to 20%.



1. INTRODUCTION

Halogen bonding (XB) is a noncovalent interaction between a halogen atom and an electron donor (Lewis base). Perhaps, the most elegant interpretation of the counterintuitive attraction in XB is based on the concept of a σ -hole, which reflects the fact that electron distribution around the halogen atom is not uniform.¹ Besides the expected negative region of electrostatic potential at the belt of the atom, there is also the region of positive potential (σ -hole), which is localized at the top of a halogen atom covalently bound to another atom. Generally, the magnitude of the σ -hole increases with the increasing atomic number of the halogen.^{1,2}

The XB is reasonably strong because of the attractive electrostatic interaction between the positive σ -hole of the halogen and an electron-rich donor (e.g., carbonyl oxygen or an aromatic ring). As shown in our previous papers, symmetry-adapted perturbation theory (SAPT) has revealed that a substantial part of the attraction comes from dispersion energy, which is caused by a close arrangement of two heavy atoms (halogen and an electron donor) with high polarizability.^{3,4} Their respective distance is often significantly shorter than the sum of their van der Waals radii. The close contact between the two atoms is responsible for the high dispersion energy of this atom pair, which is almost one-half of the total dispersion energy of the interacting molecules. This may seem surprising at first sight.

The large stability of several halogen-bonded complexes with molecular iodine (as well as with other electron acceptors), recently investigated in our laboratory, has been explained by important charge-transfer energy.⁵ It has been concluded⁶ that the significant stabilization of halogen-bonded complexes in these particular complexes is a result of the concert action of

electrostatic, induction (covering the charge-transfer), and dispersion energies in the SAPT sense. The importance of the second and third energy terms arises from the fact that the distance between the halogen atom and the electron donor is short.

The search for the origin of this remarkably short distance between heavy atoms leads to the investigation of electron densities of halogenated molecules. These studies have revealed that electron density is not spherically symmetric around the halogen but is flattened.⁷ This so-called polar flattening has been known for a long time, and it is a consequence of the fact that the halogen atom is covalently bound to another atom.⁸ It must be added here that the effect of polar flattening is not limited to halogens, but it exists for any atom that is covalently bound to another one. The flattening of the spherical electron density of an isolated atom occurs in the direction of covalent bond, and it is pronounced at most in the case of monovalent atoms. The flattened electron density at the opposite side of the covalent bond leads to a reduced repulsion with the partner approaching the halogen in this direction. As a consequence, the distance between the two atoms is reduced, which turns into a modified attraction caused by distance-dependent electrostatic, dispersion, and induction interactions.

The aim of the present study is to determine the reduction of the intermolecular distance caused by the polar flattening and, subsequently, to investigate the impact of this effect on the stability of model halogen-bonded complexes. Thus, we compare a hypothetical situation, where atoms are spherically

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symmetric, with the real situation, where atoms are flattened because of their covalent bond.

In this study, we have examined complexes of the following dihalogens: FBr, ClBr, Br₂, and IBr with electron donors: Ar, Kr, F[−], Cl[−], Br[−], I[−], HF, and HCl. The complexes of dihalogens with noble gases and anions were considered in their linear structure (cf. Figure 1A, where the Br atom was always the

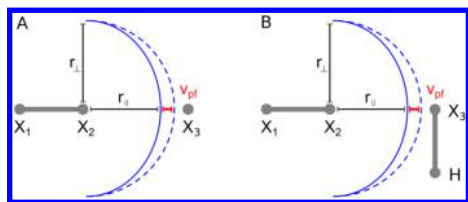


Figure 1. Schematic illustration of the polar flattening of the isodensity surface. The solid blue line stands for the real surface, the hypothetical spherical surface is in dashed blue. Halogen atoms X₁ and X₂ are in gray. Two distances r_{\perp} (perpendicular) and r_{\parallel} (parallel) determine the absolute value of polar flattening v_{pf} (in red). For clarity, the distances are not proportional; A: linear structure X₃ = Ar, Kr, F[−], Cl[−], Br[−] or I[−]; B: L-shape structure X₃ = F or Cl.

closer one to the electron donor), as this arrangement represents the binding motif utilized via the σ -hole on the Br atom. Moreover, this linear structure is the global energetic minimum for all considered complexes. The complexes of dihalogens with HF and HCl molecules were considered in the L-shaped structure (cf. Figure 1B, where the Br atom was always the closer one to the fluorine or chlorine atom), because in this arrangement we can talk about a halogen bond between the molecules. The Cartesian coordinates and the benchmark interaction energies of all of the complexes are available in the www.begdb.com⁹ online database.

2. METHODS

Geometries. The isolated molecules were subjected to geometry optimization at the B97-D/def2-QZVP level of theory.^{10–13} The default convergence criteria of the Gaussian09¹⁴ program package were adopted (maximum force $<4.5 \times 10^{-4}$ au, root-mean-square (RMS) force $<3.0 \times 10^{-4}$ au, maximum displacement $<1.8 \times 10^{-3}$ au, RMS displacement $<1.2 \times 10^{-3}$ au). Furthermore, the default thresholds, 10^{-5} au for the energy change and 10^{-7} au for the root-mean-square deviation of the density matrix, were adopted also for the SCF convergence. The grid with 75 radial shells and 302 angular points per shell was used in all density functional theory (DFT) calculations. Subsequently, unrelaxed energy scans with fixed intramolecular coordinates were utilized, in order to identify the minima on the potential energy surface of particular complexes. The main intermolecular coordinate (cf. Figure 1) was scanned in range from 1 to 10 Å, with a point-to-point distance of 0.01 Å.

Interaction Energy Calculations. The unrelaxed scans were utilized at the CCSD(T) level of theory,^{15–17} extrapolated to the complete basis set limit (CBS). The extrapolation was performed from the aug-cc-pVTZ and aug-cc-pVQZ basis sets^{18–21} by utilizing the two-point Helgaker extrapolation scheme.^{22,23} The relativistic effects were considered for the iodine atom in the form of a pseudopotential for the inner-core electrons.^{24,25} All the energies were corrected for the basis set superposition error by utilizing a counterpoise correction.²⁶

DFT-SAPT. A deeper understanding of the effect of polar flattening can be obtained by a decomposition of the total stabilization energy into a variety of energy terms. In the DFT-SAPT method,^{27–30} the interaction energy is given as a sum of electrostatic (E_1^{Pol}), exchange-repulsion (E_1^{Ex}), induction (E_2^{I}), exchange-induction, dispersion (E_2^{D}), exchange-dispersion contributions, and δHF energies. Here, the second-order exchange components are summed up with the respective induction E_2^{I} and dispersion E_2^{D} terms. The charge-transfer energy (E^{CT}) is approximated by the sum of E_2^{I} and δHF terms. The δHF term estimates higher-order Hartree–Fock contributions. We have used the PBE0AC exchange-correlation functional and aug-cc-pVTZ basis set for the decomposition. The PBE0AC functional was shown to give accurate first-order as well as induction and dispersion contributions.^{27–30} The aug-cc-pVTZ basis set is large enough to provide reliable energy components except for the dispersion one. Hence, the E_2^{D} term was scaled by a factor of 1.051 in order to estimate the CBS value.³¹ In the case of DFT-SAPT calculations presented in Table 4, no potential-energy scans have been done. The values correspond to the structures with intermolecular distances which represent the CCSD(T)/CBS energy minima enlarged by the values of polar flattening considered.

Polar Flattening. We stress that the polar flattening is a property of isolated molecules. The most commonly used approach defines the geometry effect (v_{pf}) of polar flattening as the difference between the distances of a particular isodensity surface (e.g., 0.001 au)³² from the atom nucleus in two directions: perpendicular to the covalent bond (cf. Figure 1) and along the covalent bond (cf. Figure 1).³³ However, the choice of the isodensity value, for which the polar flattening is considered (usually the above-mentioned 0.001 au), is to some extent arbitrary (see below).

In order to quantify the effect of polar flattening on the strength and geometry of a complex, the following procedure can be utilized. First, the optimal geometry for the halogen-bonded (linear) complex is found by e.g. unrelaxed scans. For this optimal geometry, the stabilization energy is evaluated. By definition, the optimized geometry is characterized by the maximal stabilization energy. In this case, the flattened electron density is inherently considered. Second, the magnitude of polar flattening can be determined from the isolated dihalogen. Subsequently, the intermolecular distance of the optimized complex is enlarged by the magnitude of the polar flattening. Finally, the stabilization energy is evaluated for the geometry with the enlarged intermolecular distance. The difference between the stabilization energies directly indicates the effect of polar flattening on the strength of the XB interaction.

In our study, we evaluated the polar flattening for two distinct values of isodensity. Namely, we have used the standard 0.001 au isodensity surface as well as the minimal isodensity surface (ρ_{min}) along the main (linear) intermolecular coordinate (cf. Figure 1). The ρ_{min} value was calculated at the PBE0AC/aug-cc-pVTZ(-PP) level,^{18–21,34,35} using cubegen utility,¹⁴ for each complex in its optimal geometry. The ρ_{min} isodensity surface can be considered as the “border” between interacting molecules (in the context of the Quantum Theory of Atoms in Molecules (QTAIM) it represents a bond critical point).³⁶ The ρ_{min} values for all investigated complexes are listed in Table 1. The ρ_{min} value was chosen because it reflects the strength of the interaction as well as the mutual polarization of electron densities between interacting molecules.

Table 1. ρ_{\min} Values (in au) for All the Complexes Investigated^a

donor, acceptor	FBr	ClBr	Br ₂	IBr
Ar	0.0084	0.0062	0.0058	0.0051
Kr	0.0100	0.0072	0.0067	0.0059
F [−]	0.0964	0.0935	0.0940	0.0907
Cl [−]	0.0608	0.0569	0.0572	0.0542
Br [−]	0.0535	0.0492	0.0495	0.0470
I [−]	0.0460	0.0423	0.0424	0.0403
HF	0.0160	0.0112	0.0098	0.0081
HCl	0.0190	0.0121	0.0109	0.0087

^aThe ρ_{\min} value corresponds to the minimum value of electron density, along the main intermolecular coordinate of the complex, in its optimal geometry.

The absolute value of the polar flattening (v_{pf}) of the monomers was defined as the difference between two distances obtained from the electron densities of isolated molecules (eq 1)

$$v_{\text{pf}} = r_{\perp} - r_{\parallel} \quad (1)$$

where r_{\perp} is the distance between the Br atom and the isodensity surface (0.001 au or ρ_{\min}) in the direction perpendicular to the X_1 - X_2 bond, and r_{\parallel} is the analogous distance in the direction of the X_1 - X_2 bond (cf. Figure 1). The relative value of polar flattening, designated as rv_{pf} is defined as the ratio between the v_{pf} and r_{\perp} values (i.e., $rv_{\text{pf}} = v_{\text{pf}}/r_{\perp}$). Note that the closer the v_{pf} and rv_{pf} values are to zero, the more spherical the isodensity surface is. In order to quantify the effect of polar flattening on the stability of the complexes, stabilization energies were evaluated for two distances. The first distance corresponds to the energy minimum, whereas the other one is increased by the respective value of polar flattening— $v_{\text{pf}}(0.001)$ or $v_{\text{pf}}(\rho_{\min})$. We believe that the presented way of obtaining the values of polar flattening as well as assessing its effects on the strength of the interaction are reasonable as they have been obtained in a consistent way.

RESULTS AND DISCUSSION

Polar Flattening. First, we discuss the polar flattening corresponding to the 0.001-au isodensity surface. The absolute and relative values of v_{pf} for FBr, ClBr, Br₂, and IBr are 0.34, 0.27, 0.25, and 0.22 Å (cf. Figure 2A), and 15, 12, 11, and 10%

(cf. Figure 2B), respectively. The v_{pf} is the largest for FBr (Br is covalently bound to the most electronegative F) and the smallest for IBr, but the variations are only modest. As mentioned above, polar flattening occurs for any two covalently bound atoms. For the sake of comparison, we present the absolute values for the hydrogen in LiH, H₂, and FH: 0.24, 0.19, and 0.35 Å. The relative values are 12, 12, and 24%, respectively.

Second, the absolute and relative values of polar flattening calculated for ρ_{\min} isodensity (Table 2) follow. Like in the case

Table 2. Absolute (in Å) and Relative (in %, in Parentheses) Values of Polar Flattening for All the Complexes Investigated^a

donor, acceptor	FBr	ClBr	Br ₂	IBr
Ar	0.23/(14)	0.19/(11)	0.18/(10)	0.16/(9)
Kr	0.22/(14)	0.19/(11)	0.18/(10)	0.16/(9)
F [−]	0.15/(15)	0.12/(12)	0.11/(11)	0.09/(9)
Cl [−]	0.16/(14)	0.13/(11)	0.12/(10)	0.10/(9)
Br [−]	0.17/(14)	0.13/(11)	0.12/(10)	0.10/(9)
I [−]	0.17/(14)	0.13/(11)	0.12/(10)	0.11/(9)
HF	0.20/(13)	0.17/(11)	0.16/(10)	0.15/(9)
HCl	0.20/(14)	0.17/(11)	0.16/(10)	0.15/(9)

^aThe values correspond to the ρ_{\min} isodensity surface.

of the 0.001 au isodensity, the largest values of both characteristics were found for the FBr diatomic molecule, where Br is bound to the most electronegative element—fluorine. Interestingly enough, the absolute v_{pf} values for the complexes of X^- , $X = \text{F, Cl, Br, and I}$ are very similar for a given diatomic monomer and lie at 0.15–0.17, 0.12–0.13, 0.11–0.12, and 0.09–0.11 (all values in Å) for FBr, ClBr, Br₂, and IBr, respectively. Comparable similarity holds for the relative v_{pf} values. For complexes with noble gases and hydrogen halides similar trends are observed. Specifically for each dihalogen, identical absolute as well as relative values of v_{pf} are obtained for Ar, Kr, HF, and HCl complexes, respectively (cf. Table 2).

The complexes of Ar and Kr exhibit larger absolute v_{pf} values than complexes with hydrogen halides or halogen anions. The v_{pf} value ranges between 0.16 and 0.23 Å. The largest absolute value was found for the FBr...Ar complex (0.23 Å or 14%, respectively). The larger absolute values of v_{pf} for Ar and Kr complexes originate in smaller ρ_{\min} values of these complexes.

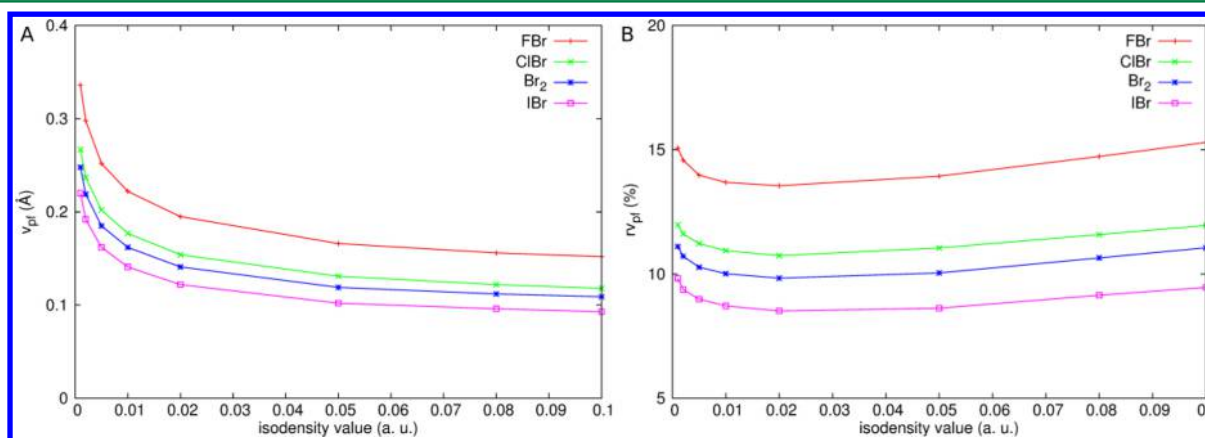


Figure 2. Dependence of the absolute polar flattening (v_{pf} panel A) and relative polar flattening (rv_{pf} panel B) on the isodensity surface value for all considered diatomics.

Figure 2 depicts the dependence of the absolute (Figure 2A) and relative (Figure 2B) values of polar flattening on the isodensity value for FBr, ClBr, Br₂, and IBr molecules. Generally, the absolute value of polar flattening decreases in the order FBr > ClBr > Br₂ > IBr. This trend is reasonable, because one would expect smaller polar flattening on halogens covalently bound to atoms with low electronegativity. Such atoms deform the halogen electron cloud to a lower extent. Furthermore, it is evident that ν_{pf} increases with the decreasing value of the underlying isodensity. The nonuniformity of electron density is introduced almost exclusively by the valence shell. As the valence-shell orbitals are more diffused than inner orbitals, they contribute more significantly to the isodensity surfaces of lower values. Hence, the polar flattening is larger when considering lower values of isodensity surface. The relative values of polar flattening do not vary as much as the absolute ones. The variations for a specific molecule do not exceed 2%. Moreover, the relative values of polar flattening for different molecules decrease in the same order as the absolute values, i.e. FBr > ClBr > Br₂ > IBr.

Putting all ν_{pf} values together, we can conclude that the absolute ν_{pf} becomes larger with a decreasing value of the underlying isodensity. However, the relative value of polar flattening is significantly less sensitive to the value of isodensity. It varies between 9 and 15% for all the complexes considered, which is in agreement with previous studies.^{7,33}

Interaction Energies. The effect of polar flattening on stabilization energy was investigated at the CCSD(T)/CBS level. Figure 3 shows stabilization energies for the equilibrium

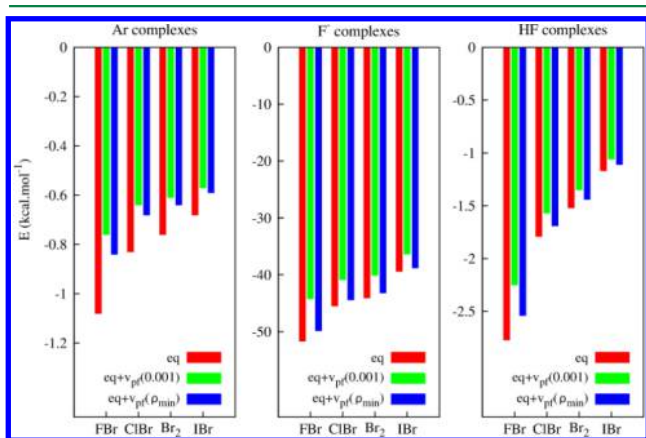


Figure 3. CCSD(T)/CBS interaction energies (in kcal·mol^{−1}) for Ar, F[−], and HF complexes calculated for the equilibrium distance (in red) and the equilibrium distance elongated by $\nu_{\text{pf}}(0.001)$ (in green) and $\nu_{\text{pf}}(\rho_{\text{min}})$ (in blue).

structures of all argon, fluoride, and hydrogen fluoride complexes (red bars), as well as for the structure where the equilibrium intermolecular distance was increased by the respective value of polar flattening ($\nu_{\text{pf}}(0.001)$ in green, $\nu_{\text{pf}}(\rho_{\text{min}})$ in blue). Evidently, this effect is not large in absolute values.

Table 3 lists the absolute and relative (in parentheses) decrease of the stabilization energy for all studied electron donors, averaged over each of the groups with four different dihalogens. The first and second columns correspond to the elongation of the equilibrium intermolecular distance by the $\nu_{\text{pf}}(0.001)$ and $\nu_{\text{pf}}(\rho_{\text{min}})$ value, respectively. The trends are comparable to those within the subgroups, i.e. the largest

Table 3. Absolute (in kcal·mol^{−1}) and Relative (in %, in Parentheses) Decrease of the Stabilization Energy for Each of the Investigated Electron Donors^a

donor, ν_{pf}	$\nu_{\text{pf}}(0.001)$	$\nu_{\text{pf}}(\rho_{\text{min}})$
Ar	0.12/(14)	0.07/(8)
Kr	0.16/(13)	0.08/(7)
F [−]	4.79/(10)	1.12/(2)
Cl [−]	2.67/(9)	0.73/(2)
Br [−]	2.30/(9)	0.64/(2)
I [−]	1.78/(7)	0.59/(1)
HF	0.26/(13)	0.12/(6)
HCl	0.30/(12)	0.14/(5)

^aThe values represent the average over the four dihalogens. The first and the second columns correspond to the enlargement of the equilibrium intermolecular distance by the $\nu_{\text{pf}}(0.001)$ and $\nu_{\text{pf}}(\rho_{\text{min}})$ value, respectively.

absolute decrease has been observed for complexes with F[−] (cf. Table 3). For the sake of completeness, we list the average values of interaction energies for subsets of complexes with different electron donors: −45.16, −28.22, −25.57, −23.06, −0.84, −1.11, −1.81, and −2.35 kcal·mol^{−1} for F[−], Cl[−], Br[−], I[−], Ar, Kr, HF, and HCl.

Regarding the relative values (cf. Table 3 in parentheses) it is evident that the effect is relatively similar and small, varying from 1 to 2% for the ρ_{min} isodensity for halide-containing complexes. This is a consequence of the shape of the stabilization energy curves with halogen anions. They are relatively deep, wide, and similar in shape. The larger relative values for Ar- and Kr-containing complexes (8 and 7%) reflect the fact that these complexes are weaker than the ionic ones. Thus, its stabilization energy profile is very shallow and narrow. Regarding complexes of hydrogen halides, their relative decrease of stabilization for ρ_{min} isodensity is somewhere between halide and noble gas containing complexes. Corresponding values are 6% (HF) and 5% (HCl). The respective relative values for the polar flattening of 0.001 au isodensity are significantly larger, likewise the increase in the intermolecular distances for such polar flattening (cf. Figure 2 and Table 3).

Finally, the F[−] complexes have the largest stabilization energies, while Ar complexes have the smallest. Their corresponding ρ_{min} values correlate well with the energies. The correlation coefficient between the ρ_{min} and the stabilization energy is 0.99. Apparently the ρ_{min} values reflect the strength of the interaction between the monomers, which is a well-known fact from the QTAIM perspective.

DFT-SAPT Decomposition. The total DFT-SAPT/CBS stabilization energies are close to the reference CCSD(T)/CBS values with the relative root-mean-square error (rRMSE) of 8%. Figure 4 depicts the DFT-SAPT/CBS decomposition of Br₂...Ar, Br₂...F[−], and Br₂...HF complexes for three intermolecular distances. Namely, the red, green, and blue bars stand for the equilibrium, $\nu_{\text{pf}}(0.001)$ and $\nu_{\text{pf}}(\rho_{\text{min}})$ elongated distances. It is evident that all attractive energy components (electrostatic, charge-transfer and dispersion) become less attractive when passing from the equilibrium to the increased distance, and, simultaneously, the repulsive term (exchange-repulsion) becomes less repulsive.

Table 4 lists the absolute and relative changes of all DFT-SAPT energy components upon the elongation of the intermolecular distance by the respective value of polar flattening (part A – 0.001 au isodensity, part B – ρ_{min}

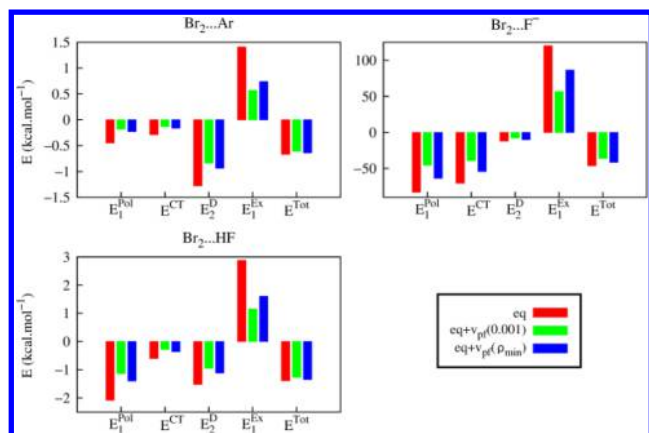


Figure 4. DFT-SAPT/CBS decomposition of the interaction energies for $\text{Br}_2\cdots\text{Ar}$, $\text{Br}_2\cdots\text{F}^-$, and $\text{Br}_2\cdots\text{HF}$ complexes calculated for the equilibrium distance (in red) and the equilibrium distance elongated by $v_{\text{pf}}(0.001)$ (in green) and $v_{\text{pf}}(\rho_{\text{min}})$ (in blue).

isodensity) for all the complexes considered. Based on the values presented, the following conclusions can be drawn. First, the changes of all separate energy terms (attractive and, more importantly repulsive) upon distance increase are much larger than the changes of the total stabilization energy. Second, the largest absolute changes are observed for complexes with F^- , as these complexes are the strongest. The moving to heavier halogen anions is connected with the decreasing value of the absolute change in all energy components. However, no such trend has been observed for the relative change. This is a consequence of the fact that all interactions between diatomic molecules and halogen anions are of the same chemical type, i.e. a diatomic molecule with a different dipole moment interacts with an anion of a different size. Third, comparing the Ar and Kr complexes, later ones are more stable. Hence their absolute changes are larger (cf. Table 4). However, relative

numbers are almost identical for both of the groups (cf. Table 4). Furthermore, the complexes of Ar have the smallest absolute changes, as these complexes are by far the weakest, although they provide the largest relative changes with the elongation of the intermolecular distance. This is caused by fact that different dipole moment interacts with a noble gas atom.

Finally, the differences in relative values for HF and HCl complexes are also negligible, as in the case of Ar versus Kr complexes. This similarity is caused by the same type of interaction between considered molecules in respective groups of complexes. Once again, the absolute values are larger for HCl complexes compared to HF ones, as former complexes are more stable.

A comparison of parts A and B of Table 4, where the numbers listed in part A correspond to the elongation of the intermolecular distance by $v_{\text{pf}}(0.001)$ and those in part B with $v_{\text{pf}}(\rho_{\text{min}})$, shows that the former ones are larger. This is understandable as geometric and consequently energetic changes based on the $v_{\text{pf}}(0.001)$ are larger than respective $v_{\text{pf}}(\rho_{\text{min}})$ values.

CONCLUSIONS

We conclude that the value of polar flattening strongly depends on the isodensity surface used for its determination. Specifically, polar flattening increases with the decreasing value of the considered isodensity. Concerning the ρ_{min} isodensity defined here as the minimum of the density lying on the path of the halogen bond, the geometrical effect of polar flattening in the XB complexes investigated reaches 0.1–0.2 Å and 9–15% for the absolute and relative values, respectively. The geometrical manifestation of polar flattening affects the stabilization energies relatively little due to a compensation of attractive and repulsive (SAPT) energy terms. The shortening of the intermolecular distance caused by the flattened ρ_{min} isodensity is responsible for the relative increase of stabilization energy by about 5–10%. Based on the isodensity of 0.001 au, the

Table 4. Absolute (in $\text{kcal}\cdot\text{mol}^{-1}$) and Relative (in %, in Parentheses) Average Change of E_1^{Pol} (Electrostatic), E^{CT} (Charge-Transfer), E_2^{D} (Dispersion), E_1^{Ex} (Exchange-Repulsion) Terms, and $E^{\text{SAPT/CBS}}$ the Total Interaction Energy Related to the Increase in the Intermolecular Distance by the Respective Value of Polar Flattening, within the Subgroups of Complexes with the Same Electron Donor

A: Elongated by $v_{\text{pf}}(0.001)$					
donor, energy	E_1^{Pol}	E^{CT}	E_2^{D}	E_1^{Ex}	$E^{\text{SAPT/CBS}}$
Ar	0.33/(−62)	0.25/(−58)	0.52/(−37)	−1.05/(−62)	0.07/(−10)
Kr	0.50/(−62)	0.40/(−58)	0.66/(−36)	−1.47/(−61)	0.12/(−11)
F^-	38.79/(−46)	31.89/(−47)	4.56/(−38)	−64.99/(−55)	10.47/(−22)
Cl^-	21.44/(−44)	16.95/(−43)	3.83/(−35)	−37.71/(−52)	4.71/(−17)
Br^-	18.88/(−43)	14.58/(−42)	3.56/(−34)	−33.38/(−51)	3.82/(−15)
I^-	16.64/(−42)	11.52/(−39)	3.32/(−33)	−28.41/(−49)	3.23/(−14)
HF	1.28/(−47)	0.51/(−57)	0.69/(−40)	2.36/(−63)	0.16/(−10)
HCl	1.72/(−49)	1.06/(−56)	1.05/(−37)	3.59/(−59)	0.29/(−12)
B: Elongated by $v_{\text{pf}}(\rho_{\text{min}})$					
donor, energy	E_1^{Pol}	E^{CT}	E_2^{D}	E_1^{Ex}	$E^{\text{SAPT/CBS}}$
Ar	0.26/(−50)	0.20/(−46)	0.39/(−28)	−0.84/(−50)	0.03/(−4)
Kr	0.39/(−49)	0.31/(−45)	0.49/(−27)	−1.16/(−48)	0.06/(−6)
F^-	20.29/(−24)	16.62/(−25)	2.26/(−19)	−34.63/(−29)	4.66/(−10)
Cl^-	11.89/(−24)	9.31/(−24)	2.02/(−19)	−21.26/(−30)	2.07/(−7)
Br^-	10.61/(−24)	8.09/(−23)	1.90/(−18)	−19.04/(−29)	1.66/(−7)
I^-	9.44/(−24)	6.39/(−21)	1.80/(−18)	−16.31/(−28)	1.41/(−6)
HF	0.92/(−34)	0.37/(−42)	0.48/(−28)	1.74/(−47)	0.05/(−3)
HCl	1.23/(−36)	0.76/(−41)	0.72/(−25)	2.61/(−44)	0.13/(−6)

geometrical effect of polar flattening is more pronounced and reaches 0.2–0.3 Å and 10–15% for the absolute and relative values, respectively. As a consequence, the shortening of the intermolecular distance caused by the flattened 0.001-au isodensity is responsible for the relative increase of stabilization energy up to 20%.

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Author Contributions

R.S., M.H.K., and P.H. designed the research, R.S. performed the calculations, and R.S., M.H.K., and P.H. interpreted the results and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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