

A computational study of the cooperativity in clusters of interhalogen derivatives

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Received: 3 October 2008 / Accepted: 20 November 2008 / Published online: 6 December 2008
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Abstract The clusters, up to four monomers, of the interhalogen derivatives (FCl, FBr, and ClBr) have been studied by means of ab initio and DFT methods, up to MP2/aug-cc-pVTZ computational methods. Two dispositions, linear and cyclic, of the clusters have been studied. Cooperative effects in the geometry, energy, and electron density have been observed in the linear and cyclic dispositions of these clusters. The Natural Energy Decomposition Analysis shows that the main source of the interaction corresponds to the polarization term.

Keywords Interhalogen · DFT · MP2 · Cooperativity · Non-pairwise effects

Introduction

Among non-covalent interactions between molecules, hydrogen bonds are doubtless the most important ones [1–7]. In recent years, new interactions where a halogen atom interacts with an electron donor atom, halogen or not, have been found to play a distinctive role in fields, such as crystal engineering [8–33] and protein–ligand interactions opening, the possibility to use them in the design of novel ligands that interact with proteins in a very specific way [34–40]. Interactions such as $-X\cdots Y-$ ($X = \text{Cl, Br, or I}$; $Y = \text{N, O, S, or } \pi$) and even as $-X\cdots Y-$ ($X = \text{Cl, Br, or I}$;

$Y = \text{Cl, Br, or I}$) also play a distinctive role in crystallography and molecular biology. These interactions have been termed *halogen bonds* (XBs).

A number of studies have shown that many properties of the halogen bond are analogous to those of the hydrogen bond [25, 27, 30, 34, 40–54]. However, only a few previous studies have focused on the theoretical study of the possible cooperativity effects on the halogen bonded clusters. Thus, a theoretical study of the cluster formed by formaldehyde with up to six molecules of FCl has been reported; the results show a shortening of the intermolecular distances as the number of FCl molecules increases [52]. The crystal structure of 1-methylpyrrol-2-yl trichloromethyl ketone presents $\text{Cl}\cdots\text{O}$ contacts, showing cooperative effects [55]. The cooperativity between hydrogen and halogen bonds have been explored in clusters that present both interactions of the type $X\cdots\text{HCN}\cdots Y$ [56]. A model that is able to predict the cooperativity based on the nature of X and Y has been proposed. The theoretical study of cyclic triangular bromine and iodine derivatives shows non-cooperativity for most of the complexes [57].

In the present article, initially the electronic characteristics of the isolated interhalogen derivatives (FCl, FBr, and ClBr) have been studied. In addition, the dimer, trimer, and tetramers in linear and cyclic configurations have been computed. The electronic results have been analyzed based on the Atoms in Molecules (AIM) methodology. The nature of the interaction has been explored using the natural energy decomposition analysis (NEDA).

Electronic supplementary material The online version of this article (doi:10.1007/s11224-008-9392-x) contains supplementary material, which is available to authorized users.

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Methods

The geometry of the systems has been initially optimized at the MP2/6-311++G(d,p) [58, 59] computational level.

Frequency calculations at this computational level have been performed to confirm that the structures obtained correspond to energetic minima. Further optimization has been performed with the M05-2x/6-311++G(d,p) [60], M05-2x/aug-cc-pVTZ [61], and MP2/aug-cc-pVTZ computational methods. All these calculations have been carried out within the Gaussian-03 package [62].

The interaction energy has been calculated as the difference between the total energy of the complexes minus the sum of the energies of the isolated monomers. The basis sets used in this work are of sufficient quality that basis set superposition errors (BSSEs) should be rather small [63]. Moreover, it has been shown that uncorrected MP2/aug-cc-pVTZ binding energies lie between corrected and uncorrected MP2/aug-cc-pVQZ energies [64]. BSSE corrections may not always improve binding energies of weakly bonded complexes, since in the counterpoise method [65], a monomer may utilize the valence and core functions of its partner, which are not available to the monomer in the complex.

The electron density topology and atomic properties have been evaluated within the AIM methodology [66] with the AIMPAC [67] and Morphy98 programs [68]. The calculation of the atomic properties has been carried out by integration within the atomic basins using the default parameters except in those cases where the integrated Laplacian was larger than 1×10^{-3} where more tight conditions have been used. Previous reports have shown small errors in the energy and charge for systems where all the values of the integrated Laplacian were smaller than the mentioned value [69].

The orbital interactions have been analyzed within the natural bond orbital (NBO) [70] framework and the NBO 5.G program [71]. This method allows the analyses of the interaction between filled and empty orbitals and associates them to charge-transfer processes. In addition, the NEDA [72, 73] has been used to obtain insights of the source of the interactions. These calculations have been performed within the Gamess program [74].

Results and discussions

Monomers

The geometry and dipole obtained for the isolated monomers calculated and those reported experimentally from microwave spectroscopy have been gathered in Table 1. The results obtained with the aug-cc-pVTZ basis set are in good agreement with the experimental data available while those with the 6-311++G(d,p) one provide longer distances than the experimental ones and larger dipole moments.

The possibility that the electron density distribution of the halogen atom presents a “polar flattening” has been proposed by Gajda and Katrusiak [20, 79, 80] based on a X-ray study of dichloroacetic acid under pressure. It was observed that one of the Cl...Cl distances (the most linear one) decreases from 3.813 Å (0.1 GPa) to 3.442 Å (1.4 GPa). We have evaluated the effective radius of the halogen atoms in these compounds in the axial direction and in the perpendicular one. The calculated distances from the atomic position to the 0.001 e/bohr³ isosurface in both directions have been gathered in Table 2. For comparative purposes, the values obtained for the homohalogen molecules have been included. In all the cases, the effective radius in the axial direction is smaller than in the perpendicular one. The electronegativity of the neighboring atom clearly influence the values obtained. Thus, in all the cases, the values are smaller, for a given atom, when it is bonded to fluorine and larger when it is bonded to bromine.

Among the electrostatic properties of the isolated monomers, the value of the molecular electrostatic potential (MEP) has been widely used to predict the formation of complexes. In the molecules considered here, an almost perfect linear correlation is found between the MEP and the dipole moment (Fig. 1).

Table 1 Calculated and experimental bond distances (Å) and dipole moments (Debye) of the interhalogen molecules considered here

	M052x/6-311++G(d,p)		M052x/aug-cc-pVTZ		MP2/6-311++G(d,p)		MP2/aug-cc-pVTZ		Experimental	
	Dist.	Dip.	Dist.	Dip.	Dist.	Dip.	Dist.	Dip.	Dist.	Dip.
FCI	1.645	1.317	1.622	0.969	1.673	1.345	1.638	0.916	1.628 ^a	0.888 ^b
FBr	1.781	1.815	1.751	1.423	1.807	1.828	1.758	1.324	1.759 ^a	1.422 ^c
ClBr	2.166	0.430	2.146	0.386	2.166	0.518	2.138	0.449	2.136 ^a	0.519 ^d

^a Taken from ref. [75]

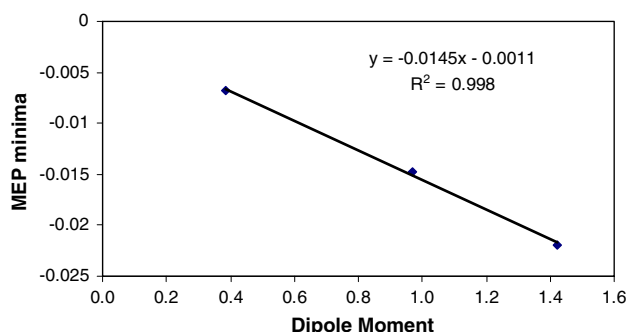
^b Taken from ref. [76]

^c Taken from ref. [77]

^d Taken from ref. [78]

Table 2 Effective atomic radius (Å) in the axial and perpendicular directions

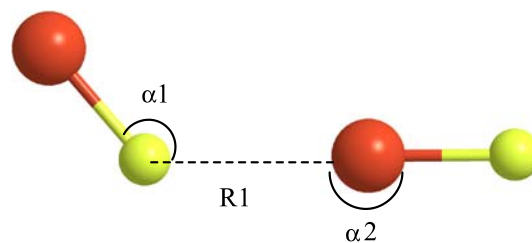
XY molecules	X (axial)	X (perp)	Y (axial)	Y (perp)
FCI	1.586	1.707	1.817	2.118
FBr	1.601	1.718	1.914	2.246
ClBr	1.903	2.135	1.981	2.257
F ₂	1.527	1.678		
Cl ₂	1.883	2.130		
Br ₂	2.000	2.261		

**Fig. 1** Dipole moment (Debye) versus MEP minima (a.u.) of the interhalogen molecules calculated at the M05-2x/aug-cc-pVTZ computational level

Dimers

The geometry of the complexes is gathered in Table 3 and represented in Fig. 2. To the best of our knowledge, the only experimental data available for these complexes correspond to a symposium communication of the FCI dimer [81] where only the rotational constants are provided and thus, no direct comparison is possible. The calculated geometries present a non-linear disposition with a $\alpha 1$ angle that varies between 92 and 110° at MP2/aug-cc-pVTZ computational level. In all the cases, the calculated $\alpha 2$ angle is very closed to 180°. The structures obtained resemble that of the HF dimer.

The interatomic distances obtained for these complexes are shorter than the corresponding atomic radius previously calculated as indication of electronic overlap of the two monomers. A similar tendency has been proposed to be a

**Fig. 2** Optimized geometry of the (FBr)₂ at the MP2/6-311++G(d,p) computational level with indication of the parameters used to define the geometry

characteristic of the hydrogen bonds. The dimer formation produces a small elongation of the monomer that acts as electron acceptor up to 0.008 Å in the ClBr dimer. Associated to this elongation of the bond length, a red shift in the corresponding stretching is observed (6, 7, and 3 cm⁻¹ for the FCI, FBr, and ClBr dimers, respectively).

The calculated interaction energies of the dimers are reported in Table 4. With the 6-311++G(d,p) basis set at the two computational methods considered here, the interaction energy follows the order observed in the dipole moment of the monomers, while with the aug-cc-pVTZ basis set, the largest interaction energy is obtained for the FBr dimer, followed by the ClBr one and the least stable one is (FCI)₂.

It is noteworthy the large difference in the interaction energy of the ClBr dimer obtained at the MP2/aug-cc-pVTZ computational level when compared to the rest of the methods considered here. For this reason, we have decided to explore the results obtained for that dimer with other basis sets and computational methods (Table 5). The results at MP2 level indicate similar results for the three correlation consistent basis sets considered here. In addition, the slightly larger interaction energy obtained at the

Table 4 Interaction energy (kJ mol⁻¹) of the dimers

	M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
(FCI) ₂	-11.59	-7.51	-9.71	-8.43
(FBr) ₂	-15.68	-13.31	-13.85	-15.66
(ClBr) ₂	-7.98	-8.53	-8.55	-14.70

Table 3 Intermolecular parameters of the calculated dimers

		M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
(FCI) ₂	R1	2.689	2.812	2.765	2.746
(FCI) ₂	$\alpha 1$	124.2	122.0	131.2	110.5
(FBr) ₂	R1	2.634	2.656	2.765	2.686
(FBr) ₂	$\alpha 1$	133.7	121.1	129.7	114.8
(ClBr) ₂	R1	3.353	3.275	3.405	3.152
(ClBr) ₂	$\alpha 1$	99.5	96.8	101.6	92.5

Table 5 Interaction energy and geometry of the ClBr dimer calculated at different computational levels

Comp. level	Ei (kJ mol ⁻¹)	R1 (Å)	α 1 (°)
MP2/aug-cc-pVDZ	-14.20	3.205	92.4
MP2/aug-cc-pVTZ	-14.70	3.152	92.5
MP2/aug-cc-pVQZ	-15.30	3.130	91.1
MP4/aug-cc-pVDZ	-10.00	3.330	93.0
MP4/aug-cc-pVTZ	-9.24	3.339	92.4
CCSD/aug-cc-pVDZ	-9.83	3.337	93.0

MP2/aug-cc-pVQZ computational level in comparison to the MP2/aug-cc-pVTZ one confirms the no need to include BSSE in these calculations. However, the inclusion of larger correlation as MP4 or CCSD decreases significantly the interaction energy. For comparative purposes, the calculated interaction energies of the FCl and FBr dimers at the MP4/aug-cc-pVTZ are -7.7 and -14.0 kJ mol⁻¹, respectively.

The intermolecular distances obtained at the different computational levels parallels the interaction energies; thus, larger interaction energies correspond to shorter distances.

The analysis of the electron density of the complexes shows the presence of a bond critical point (BCP) with small values of the electron density and positive values of the Laplacian as indication of the closed shell nature of the interaction (Table 6). The integrated properties within the atomic basins shows a small charge transfer between the two molecules, an energy stabilization slightly larger in the electron acceptor molecule than in the electron donor and a reduction of the molecular volume.

The NBO shows the presence of an orbital interaction of the lone pair of the e-donor molecule with the σ^* of the electron acceptor (Table 7). This kind of interaction is mainly responsible for the stabilization energy found in hydrogen bonded clusters [70]. The NEDA indicates that the main important stabilization term is the polarization one, followed by the charge transfer. In contrast, the most important term in hydrogen bonded systems, as in water clusters, is the charge transfer [73]. The energy destabilization due to the electronic deformation is larger in the electron donor molecule than in the electron acceptor.

Table 6 Properties of the intermolecular BCP (a.u.), charge transfer (e), energy (kJ mol⁻¹) and total volume (a.u.) variation upon complexation obtained with the AIM methodology using the MP2/6-311++G(d,p) computational level

	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	Charge transfer	ΔE (e-acceptor)	$\Delta \text{Vol.}$
(FCl) ₂	0.012	0.055	-0.0018	-8.30	-7.0
(FBr) ₂	0.014	0.060	-0.0007	-8.01	-11.2
(ClBr) ₂	0.008	0.031	0.0119	-9.77	-3.5

Table 7 Energetic value of the electron donor lone pair $\rightarrow \sigma^*$ of the electron acceptor and values of the NEDA components (kJ mol⁻¹) using the NBO methodology

	(FCl) ₂	(FBr) ₂	(ClBr) ₂
lp $\rightarrow \sigma^*$	5.9	20.2	15.5
Charge transfer	-14.4	-30.8	-22.3
Electrostatic	-6.7	-17.9	-9.4
Polarization	-27.0	-79.6	-60.2
Exchange	-11.5	-25.7	-20.7
Deformation e-donor	31.3	85.6	70.1
Deformation e-acceptor	21.5	56.0	35.0

Trimers and tetramers

Two configurations have been explored for the trimers and tetramers. The first one corresponds to a linear zig-zag disposition and the second one is a cyclic arrangement (Fig. 3). The geometrical characteristics of the trimers have been gathered in Table 8. In all the linear clusters, the intermolecular distances obtained in these cases are shorter than the corresponding ones in the dimers, being R1 shorter than R2. The larger effect is observed in the (FBr)₃ where R1 shortens 0.062 Å and R2 0.043 Å at the MP2/6-311++G(d,p) computational level. Similar results have been described for the linear trimers of HCN and HNC [82]. These results have been assigned to a cooperativity in the association.

In contrast, the intermolecular distances observed in the cyclic configuration are larger than those found in the dimers probably due to the non-optimal pairwise disposition that is partially compensated by having three interactions versus the two found in the linear clusters. Again, similar results have been obtained in HCN and HNC cyclic clusters [83].

The interaction energies obtained for the cyclic and linear trimers are reported in Table 9. For the trimer of FCl and FBr, the linear structure is more stable than the cyclic one while the opposite happens with the ClBr trimer. The dependence of the energetic results with the computational method and basis set used are similar to those already described for the dimers.

The values obtained in the linear trimers are, in absolute value, larger than twice of the corresponding dimers calculated at the same computational level, being the larger difference 3.0 kJ mol⁻¹ for the FBr trimer calculated at the MP2/6-311++G(d,p) computational level. The calculated interaction of the first and last monomer in the chain, as they stand in the cluster, is always smaller than this difference (0.6 kJ mol⁻¹ in the FBr cluster) and thus, the energetic results confirm the cooperativity observed in the geometry.

Fig. 3 Optimized geometries of the $(\text{FBr})_3$ at the MP2/6-311++G(d,p) computational level with indication of the parameters used to define the geometry

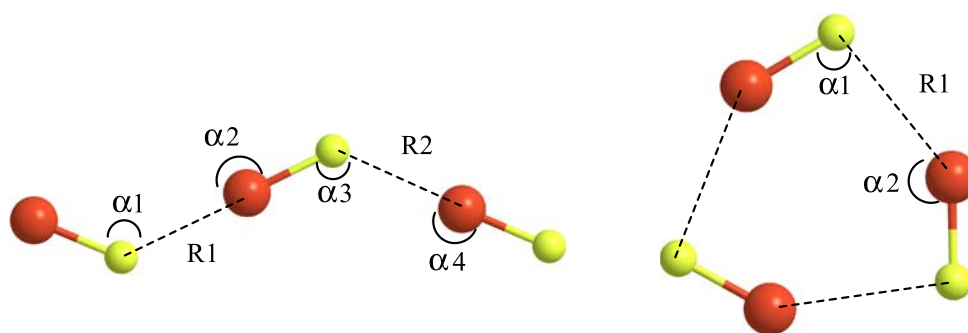


Table 8 Geometry (\AA , $^\circ$) of the trimers

		M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
$(\text{FCl})_3$ (linear)	R1	2.626	2.664	2.731	2.711
	R2	2.629	2.684	2.739	2.726
	$\alpha 1$	125.3	125.1	129.8	111.5
	$\alpha 2$	130.5	129.8	131.4	110.6
$(\text{FBr})_3$ (linear)	R1	2.612	2.629	2.703	2.625
	R2	2.616	2.687	2.722	2.648
	$\alpha 1$	128.8	116.7	129.9	115.3
	$\alpha 2$	124.1	115.3	129.5	114.7
$(\text{ClBr})_3$ (linear)	R1	3.305	3.214	3.373	3.102
	R2	3.329	3.244	3.392	3.130
	$\alpha 1$	99.9	96.5	101.2	93.7
	$\alpha 2$	96.9	93.8	99.8	91.4
$(\text{FCl})_3$ (cyclic)	R1	2.989	3.204	3.130	3.101
	$\alpha 1$	95.4	91.6	96.3	92.9
	$\alpha 2$	144.6	148.4	143.7	147.1
$(\text{FBr})_3$ (cyclic)	R1	3.044	3.077	3.214	3.095
	$\alpha 1$	98.3	95.6	97.5	94.3
	$\alpha 2$	141.7	144.4	142.5	145.7
$(\text{ClBr})_3$ (cyclic)	R1	3.447	3.371	3.579	3.292
	$\alpha 1$	85.4	82.6	85.0	82.8
	$\alpha 2$	154.6	157.4	155.0	157.2

Table 9 Interaction energy of the calculated trimers (kJ mol^{-1})

	M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
$(\text{FCl})_3$ (cyclic)	−21.03	−14.43	−18.09	−16.54
$(\text{FCl})_3$ (linear)	−24.65	−14.77	−21.12	−17.82
$(\text{FBr})_3$ (cyclic)	−25.77	−21.84	−22.34	−28.86
$(\text{FBr})_3$ (linear)	−35.93	−27.90	−30.68	−34.14
$(\text{ClBr})_3$ (cyclic)	−21.19	−21.24	−20.90	−38.54
$(\text{ClBr})_3$ (linear)	−17.33	−18.15	−18.09	−31.20

The AIM analysis presents bcp's in the linear trimers with larger values of the ρ and $\nabla^2\rho$ than those corresponding to the dimers while the opposite happens with the cyclic ones (Table 10). The integrated energy in the monomers indicates that their stabilization increases from

the initial electron donor molecule to the final electron acceptor one as we move along the chain.

The NBO and NEDA analysis (Table 11) show an increment in the orbital interaction between the monomers with respect to the one observed in the dimers in the linear

Table 10 Properties of the intermolecular BCP (a.u.), and energy variation (kJ mol^{−1}) upon complexation obtained with the AIM methodology using the MP2/6-311++G(d,p) computational level

	ρ_{BCP} (R1)	$\nabla^2 \rho_{\text{BCP}}$ (R1)	ρ_{BCP} (R2)	$\nabla^2 \rho_{\text{BCP}}$ (R2)	ΔE (Mon-1)	ΔE (Mon-2)	ΔE (Mon-3)
(FCl) ₃ (linear)	0.013	0.059	0.013	0.058	−2.7	−7.2	−11.1
(FBr) ₃ (linear)	0.016	0.068	0.016	0.066	−6.4	−11.5	−12.6
(ClBr) ₃ (linear)	0.009	0.032	0.008	0.031	2.5	−9.1	−11.1
(FCl) ₃ (cyclic)	0.007 ^a	0.031			−6.0	−6.0	−6.0
(FBr) ₃ (cyclic)	0.007 ^a	0.030			−7.4	−7.4	−7.4
(ClBr) ₃ (cyclic)	0.006 ^a	0.023			−7.0	−7.0	−7.0

^a The properties of the three intermolecular BCP are identical

Table 11 Energetic value of the electron donor lone pair $\rightarrow \sigma^*$ of the electron acceptor and values of the NEDA components (kJ mol^{−1}) using the NBO methodology in the trimers

	(FCl) ₃ (linear)	(FBr) ₃ (linear)	(ClBr) ₃ (linear)	(FCl) ₃ (cyclic)	(FBr) ₃ (cyclic)	(ClBr) ₃ (cyclic)
lp $\rightarrow \sigma^*$ (1)	10.3	24.3	17.74	1.21	3.77	10.21
lp $\rightarrow \sigma^*$ (2)	8.9	20.1	16.07	1.21	3.77	10.25
Charge transfer	−41.3	−65.4	−53.8	−21.4	−35.1	−50.8
Electrostatic	−19.0	−37.9	−24.6	−13.1	−34.8	−30.0
Polarization	−86.9	−169.8	−128.4	−32.3	−112.7	−174.1
Exchange	−33.0	−53.1	−41.8	−24.2	−48.5	−67.3
Total deformation	166.0	299.1	233.8	78.0	210.5	303.8

Table 12 Geometric results tetramers

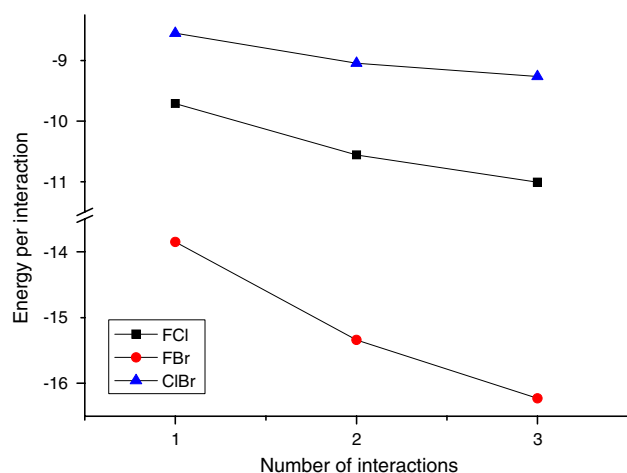
		M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
(FCl) ₄ (linear)	R1	2.627	2.738	2.723	2.701
	R2	2.603	2.688	2.703	2.689
	R3	2.643	2.763	2.732	2.720
	$\alpha 1$	122.8	110.6	129.7	111.8
	$\alpha 2$	124.4	119.0	129.5	111.4
	$\alpha 3$	123.5	109.4	131.2	110.8
(FBr) ₄ (linear)	R1	2.577	2.616	2.684	2.606
	R2	2.560	2.583	2.652	2.582
	R3	2.594	2.654	2.707	2.635
	$\alpha 1$	133.6	123.6	130.0	115.8
	$\alpha 2$	128.5	118.7	129.0	115.6
	$\alpha 3$	134.2	121.5	129.7	114.9
(ClBr) ₄ (linear)	R1	3.284	3.210	3.369	3.092
	R2	3.316	3.226	3.357	3.073
	R3	3.337	3.240	3.384	3.121
	$\alpha 1$	102.1	100.2	102.0	93.6
	$\alpha 2$	94.5	95.7	99.7	92.8
	$\alpha 3$	95.6	96.8	100.0	92.0
(FCl) ₄ (cyclic)	R1	2.688	2.759	2.814	2.757
	$\alpha 1$	104.5	101.9	105.5	101.1
	$\alpha 2$	165.5	168.1	164.5	168.9
(FBr) ₄ (cyclic)	R1	2.662	2.708	2.790	2.665
	$\alpha 1$	105.4	103.3	105.8	102.2
	$\alpha 2$	164.6	166.7	164.2	167.8

Table 12 continued

		M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
(ClBr) ₄ (cyclic)	R1	3.288	3.167	3.356	3.031
	α 1	95.3	93.7	95.6	93.1
	α 2	174.7	176.3	174.4	176.9

Table 13 Interaction energy of the tetramer (kJ mol⁻¹)

	M05-2x/6-311++G(d,p)	M05-2x/aug-cc-pVTZ	MP2/6-311++G(d,p)	MP2/aug-cc-pVTZ
(FCl) ₄ (cyclic)	-49.51	-34.45	-38.40	-36.30
(FCl) ₄ (linear)	-38.71	-25.36	-33.03	-27.54
(FBr) ₄ (cyclic)	-72.04	-59.87	-55.75	-69.37
(FBr) ₄ (linear)	-57.32	-45.64	-48.69	-53.72
(ClBr) ₄ (cyclic)	-38.03	-39.34	-38.41	-68.68
(ClBr) ₄ (linear)	-26.30	-26.93	-27.79	-48.06

**Fig. 4** Interaction energy per interaction (kJ mol⁻¹) versus the number of interaction in the FCl, FBr, and ClBr clusters in linear configuration

configuration. In the same way, a significant increment in the different component of the NEDA analysis is observed, up to three times in the linear configuration. Anyhow, the polarization term is the most important attractive contribution for all the cases studied here.

The results obtained for the tetramers are in general similar to the ones already described and discussed in the trimers; and thus, the geometric and energetic results will be considered briefly. The geometric and energetic results of the tetramers are gathered in Tables 12 and 13, respectively. The linear tetramers present the central interaction (R2) being the shortest, followed by the first one (R1) and the last the longest (R3). R2 is shorter than any of the intermolecular distances reported for the dimers in Table 8 at the same computational level for the same compound. Similar results have been described in hydrogen bonded clusters [84, 85].

In the tetramers, the cyclic configuration is more stable than the linear one in the three cases considered here. Both linear and cyclic configurations presents cooperative effect as can be seen in Fig. 4.

Conclusions

A theoretical study of the properties of the monomers, dimers, trimers, and tetramers of the interhalogen molecules (FCl, FBr, and ClBr) has been carried out by means of ab initio (MP2) and DFT (M05-2X) computational methods. The results have allowed to analyze the characteristics of the monomers and clusters up to tetramers. In the trimers and tetramers, two configurations have been explored, a linear and a cyclic one. In the trimers, the linear configuration is the most stable one for FCl and FBr molecules, while for the ClBr trimers and all the tetramers the cyclic configuration is more stable.

The geometrical, electronic, and energetic parameters obtained show the presence of cooperativity in the larger clusters. The NEDA shows that the most important attractive term corresponds to the polarization one.

Acknowledgments This work was carried out with financial support from the Ministerio de Educación y Ciencia (Project No. CTQ2007-61901/BQU) and Comunidad Autónoma de Madrid (Project MADRISOLAR, ref. S-0505/PPQ/0225). Thanks are given to the CTI (CSIC) for allocation of computer time.

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