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Charge-Transfer Complexes between Dihalogen Compounds and Electron Donors

Ibon Alkorta,* Isabel Rozas, and José Elguero

Instituto de Química Médica (C.S.I.C.), Juan de la Cierva, 3, 28006-Madrid, Spain

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A theoretical study of the charge-transfer complexes formed by dihalogen compounds (F_2 , Cl_2 , Br_2 , FBr , FCI , and $ClBr$) and electron donors (FH , OH_2 , NH_3 , CO , NCH , and C_2H_2) has been carried out. The geometries, energies, and electronic and spectroscopic properties of these complexes have been compared with the corresponding properties of the hydrogen bonded complexes of FH with the same electron donors. The hybrid HF-DFT, B3LYP, and second-order Møller–Plesset perturbation, MP2, methods have been used. The properties analyzed include geometry, energy, electron distribution using the atoms in molecules (AIM) methodology, and spectroscopic constants of the complexes and monomers. Similarities in the variations of the geometries, in the trends in the interaction energetic, and in the topological electron density characteristics between the properties of the HB complexes and the dihalogen charge-transfer systems are pointed out. The main differences correspond to the variation trend of the atomic properties and the NMR shielding when going from the monomers to the complexes.

Introduction

The charge-transfer complexes, as defined by Mulliken¹ in 1969, include a number of situations as the hydrogen bonds (HBs) and complexes where a halogen atom acts as an electron acceptor (named in this article as halogen bonded (HalB) complexes in homology to the HB ones). These interactions have been shown to be important in different molecular recognition processes such as crystal packing.^{2,3}

While much effort has been devoted to the study of HB complexes, extending the possible electron donor (carbenes,^{4,5} isocyanides,⁶ radicals,^{7,8} π -systems,⁹ and metal hydrides^{10,11}) and electron acceptor groups (C–H moiety^{12,13}), experimental studies of charge-transfer HalB complexes have been limited, for experimental reasons, mostly to complexes with iodine. More recently, the development of new methods for interrupting the vigorous reaction of hydrogen compounds with halogens has allowed characterization of a number of pre-reactive HalB complexes, using Fourier transform microwave spectroscopy, where the interacting halogen atom includes bromine, chlorine, and fluorine.^{14,15}

A number of theoretical studies have focused their attention on these kinds of interactions. Thus, in 1950 Mulliken theoretically and experimentally examined the complexes between halogen molecules and aromatic and oxygenated solvents.¹⁶ The experimental description of the “anti-hydrogen bonded” complexes of FH with dihalogen molecules in the 1980s produced a theoretical study of the relative stability of the HB and HalB complexes of these molecules.¹⁷ More recently, the complex formed by $BrONO_2 \cdots H_2O$ was shown to be a nearly linear $O-Br \cdots O$ configuration, as the authors note “like in conventional HBs”.¹⁸ The natural bond orbital (NBO) analysis indicates a charge transfer from the acetylene to the FCI molecule and a $\pi_{C-C} \rightarrow \sigma^*_{CIF}$ donor–acceptor interaction as the source of the charge transfer for the acetylene–chlorine monofluoride ($C_2H_2 \cdots ClF$) system.¹⁹ Finally, calculations

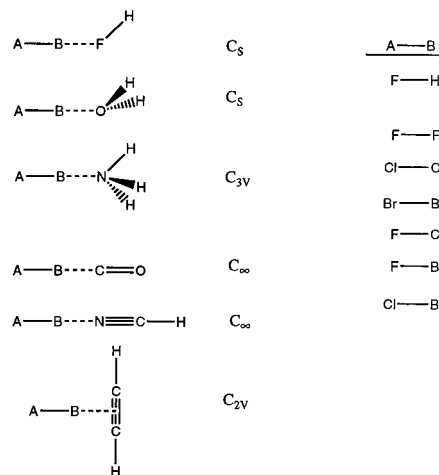


Figure 1. Schematic representation of the complexes studied.

performed on the I_2 –pyridine²⁰ systems show a binding energy of about 9 kcal/mol and a charge transfer between 0.2 and 0.3 e .

In the present article, the complexes formed by six dihalogen molecules (FF , $ClCl$, $BrBr$, FCI , FBr , and $ClBr$) with six electron donor molecules (FH , OH_2 , NH_3 , CO , NCH , and C_2H_2) have been studied using hybrid HF-DFT (B3LYP) and MP2 methods. A comparative analysis of the properties of the present complexes with the parallel HB series formed by $F-H$ and the six electron donor monomers has been carried out.

Methods

The charge-transfer complexes formed by six dihalogen molecules (FF , $ClCl$, $BrBr$, FCI , FBr , and $ClBr$) with six electron donor molecules (FH , OH_2 , NH_3 , CO , NCH , and C_2H_2) have been studied as shown in Figure 1. The less electronegative atom of the dihalogen molecule has been pointed toward the electron rich center of the electron donor molecules in order to generate a favorable dipole–dipole interaction.

* To whom correspondence should be addressed. Fax: 34-91-564 48 53. E-mail: ibon@pinar1.csic.es.

TABLE 1: Calculated and Experimental Intermolecular Distances (Å) and the Experimental Intermolecular Stretching Constants, k (N/m)

	B3LYP/6-31G*	B3LYP/6-311++G**	MP2/6-311++G**	expt	k	exptl data taken from given ref
FH...FH			1.874			
FH...OH ₂			1.730			
FH...NH ₃			1.703			
FH...CO			2.132			
FH...NCH			1.887			
FH...HCCH			2.186			
FF...FH	2.422	2.666	2.713			
FF...OH ₂	2.387	2.356	2.641	2.719	3.6	32
FF...NH ₃	2.214	1.986	2.594	2.708	4.69	33
FF...CO	2.701	2.765	3.005			
FF...NCH	2.680	2.668	2.805	2.803	2.61	34
FF...HCCH	2.596	2.481	2.901			
ClCl...FH	2.658	2.875	2.917	2.960	4.5	35
ClCl...OH ₂	2.578	2.667	2.780			
ClCl...NH ₃	2.384	2.448	2.621	2.730	12.71	36
ClCl...CO	2.913	3.048	3.180	3.134	3.7	37
ClCl...NCH	2.812	2.860	2.920	2.917	6.5	38
ClCl...HCCH	2.927	3.031	3.173	3.163	5.6	37
BrBr...FH	2.731	2.964	3.161			
BrBr...OH ₂	2.629	2.733	2.823			
BrBr...NH ₃	2.492	2.551	2.624	2.720	18.5	39
BrBr...CO	2.881	3.090	3.208			
BrBr...NCH	2.850	2.900	2.939			
BrBr...HCCH	2.944	3.093	3.193			
FCl...FH	2.531	2.668	2.777	2.760	7.23	40
FCl...OH ₂	2.454	2.457	2.588	2.575	14.2	41
FCl...NH ₃	2.337	2.277	2.312	2.370	34.3	42
FCl...CO	2.640	2.597	2.937	2.770	7.03	43
FCl...NCH	2.631	2.559	2.698	2.639	12.25	44
FCl...HCCH	2.754	2.787	2.958	2.869	9.98	45
FBr...FH	2.547	2.713	2.816			
FBr...OH ₂	2.487	2.501	2.572			
FBr...NH ₃	2.385	2.361	2.358			
FBr...CO	2.388	2.317	2.759			
FBr...NCH	2.540	2.505	2.625			
FBr...HCCH	2.749	2.740	2.878			
ClBr...FH	2.635	2.884	2.961			
ClBr...OH ₂	2.576	2.655	2.765			
ClBr...NH ₃	2.431	2.490	2.570	2.672	26.7	46
ClBr...CO	2.748	2.927	3.136	3.004	6.18	46
ClBr...NCH	2.749	2.794	2.874	2.834	11.2	47
ClBr...HCCH	2.867	2.996	3.134	3.059	9.4	46

The geometries of the monomers and the complexes have been fully optimized with the program Gaussian-94²¹ using the standard 6-31G*²² and 6-311++G**²³ basis sets and the hybrid Hartree–Fock–density functional method (Becke3LYP).²⁴ Post-Hartree–Fock calculations have been carried out at the second-order Møller–Plesset (MP2) level²⁵ with the largest basis set.

In addition, the HB complexes formed by FH and the six electron donor molecules previously mentioned have been optimized at the B3LYP/6-311++G** and MP2/6-311++G** levels of theory.

The selected level of calculation allows for comparison of the B3LYP method with the MP2 one. The latter method in conjunction with an extended basis set that includes diffuse and polarization functions in all of the atoms, as the 6-311++G**, is considered adequate for the study of HB interactions²⁶ and provides results in agreement with experimental data for some HalB complexes.¹⁹

The nature of the monomers and complexes as a potential energy minimum has been established at the B3LYP/6-31G* and MP2/6-311++G** levels in all cases by verifying that the corresponding frequencies are all positive. The interaction energies, $E_i(\text{AB})$, have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers (eq 1), where $E(\text{AB})_{\text{AB}}$ represents the energy of the

complex and $E(\text{A})_{\text{A}}$ the energy of the isolated monomer A calculated with its corresponding basis set.

$$E_i(\text{AB}) = E(\text{AB})_{\text{AB}} - [E(\text{A})_{\text{A}} + E(\text{B})_{\text{B}}] \quad (1)$$

In addition, a corrected interaction energy ($E_{\text{I+BSSE}}$) excluding the inherent basis set superposition error (BSSE) has been evaluated. The BSSE has been calculated using the Boys–Bernardi counterpoise technique²⁷ and eq 2, where $E(\text{A})_{\text{AB}}$

$$E_{\text{BSSE}}(\text{AB}) = E(\text{A})_{\text{A}} - E(\text{A})_{\text{AB}} + E(\text{B})_{\text{B}} - E(\text{B})_{\text{AB}} \quad (2)$$

represents the energy calculated for monomer A using its geometry in the complex and the complete set of basis functions used to described the dimer and $E(\text{A})_{\text{A}}$ the energy for monomer A using its geometry in the complex and its basis set.

The corrected interaction energies have been calculated with eq 3.

$$E_{\text{I+BSSE}}(\text{AB}) = E_i(\text{AB}) + E_{\text{BSSE}}(\text{AB}) \quad (3)$$

The topological properties of the electronic charge density and the atomic charges have been characterized using the atoms in molecules methodology (AIM)²⁸ with the AIMPAC program package²⁹ at the MP2/6-311++G** level. The AIM methodol-

ogy self-consistently partitioned any system and its properties into its atomic fragments by considering the gradient vector field of its electron density distribution. A 0.001 e/au^3 electron density has been used to define the atomic volume.

Nuclear magnetic resonance (NMR) spectroscopic shieldings of the isolated molecules and complexes have been calculated using the gauge-independent atomic orbital (GIAO) perturbation method³⁰ as implemented in the Gaussian-94 program. This perturbation method, as suggested by London, proposes local gauge origins to define the vector potential of the external electric field.³¹

Results and Discussion

Geometry. The calculated and experimentally available intermolecular distances have been gathered in Table 1. The hybrid HF-DFT (B3LYP/6-31G* and B3LYP/6-311++G**) methods used here provide the shortest distances when compared to the MP2/6-311++G** results or to the experimental ones. The results obtained with the latter methods are the closest to the experimental ones with an average absolute error of 0.066 Å, while the corresponding error for the hybrid HF-DFT methods is 0.200 Å for B3LYP/6-31G* and 0.160 Å for B3LYP/6-311++G**.^{32–47}

The largest error obtained for the hybrid HF-DFT methods corresponds to the complexes formed between homodihalogen compounds and the electron donors. Those errors can reach values of 0.494 at B3LYP/6-31G* and 0.722 Å at B3LYP/6-311++G** for the $\text{F}_2 \cdots \text{NH}_3$. The largest error at the MP2/6-311++G** level is 0.167 Å in the $\text{FCl} \cdots \text{CO}$ complex.

The longest interacting distances always correspond to those complexes where the electron donors have the smallest dipole moments and at the same time are the weakest bases, CO and HCCH. The shortest distances correspond to the complexes with OH_2 and NH_3 . The same tendencies are observed in the HBs reported in Table 1.

The calculated bond angles in the HalBs, as well as in the HBs, defined as $\text{X}-\text{Y} \cdots \text{Z}$ (where XY is the dihalogen molecule in the HalB systems and Z the electron donor group; in the case of HCCH the center of the molecule has been considered) are almost linear in all cases. For example, the largest deviation from linearity in the $\text{X}-\text{Y} \cdots \text{Z}$ angle corresponds to the $\text{Cl}_2 \cdots \text{FH}$ and $\text{FH} \cdots \text{FH}$ systems with values of 177 and 172°, respectively.

The formation of the HalB complexes produces an elongation of the dihalogen bond. This effect is generally very small in the weakest complexes, although, it can reach values of 0.065 Å in cases such as the strong $\text{FBr} \cdots \text{NH}_3$ complex. Something similar occurs in the HB complexes. For example, the FH bond elongates by 0.03 Å on the $\text{FH} \cdots \text{NH}_3$ complex. In contrast, the geometrical perturbation on the electron donor groups is always very small, for instance in the two strong complexes mentioned above, where only a lengthening of 0.002 Å is produced in the NH bonds.

Energy. The interaction energy, BSSE correction, and corrected interaction energy have been collected in Table 2. These methods that provide the shortest distances, B3LYP/6-31G* and B3LYP/6-311++G**, are those that provide the largest interaction energies for each complex studied.

As expected, the dihalogen molecules with the largest dipole moments ($\text{FBr} > \text{FCl} > \text{ClBr}$), or in the case of homodihalogen those which are most polarizable ($\text{Br}_2 > \text{Cl}_2 > \text{F}_2$), have the largest interaction energies. Regarding the electron donor atoms, the strongest complexes are those formed with NH_3 . They are

approximately two times stronger than those of OH_2 and NCH . The weakest complexes correspond to those with FH , CO , and HCCH . The same trend is observed in the case of the HBs calculated here. The BSSE correction is especially important for these calculations with the 6-31G* basis set where it can represent, in some cases, over 75% of the uncorrected interaction energy. The smallest effects of this correction correspond to the B3LYP/6-311++G** calculations, which are not greater than 1.0 kcal/mol.

A Free–Wilson model⁴⁸ of the corrected interaction energy, $E_{\text{I+BSSE}}$, at the MP2/6-311++G** level, as a function of the different monomers involved in the complexes, can be established:

$$E_{\text{I+BSSE}} = \sum X_i Y_i$$

where the coefficients X_i are 1 if the monomer i is present and 0 if not and Y_i indicates the contribution of that monomer to $E_{\text{I+BSSE}}$. To avoid the singularity of the matrix, the correlation should be carried out with respect to a reference monomer which by definition has a Y_i coefficient equal to 0.0. In this case the reference monomer chosen is FH . The corresponding coefficients for the rest of the monomers are gathered in Table 3, and the correlation coefficient obtained is $r^2 = 0.926$ for the 36 cases studied. The values of the coefficients agree with the previous analysis of the $E_{\text{I+BSSE}}$ as a function of the monomers involved. In addition, the coefficients of the electron donors follow the same tendency as the experimental proton affinities.⁴⁹

A set of good linear correlations between the energy of the complexes for each electron donor and those obtained in the corresponding HB complexes with FH (Figure 2) is obtained:

$$E_{\text{I+BSSE}}(\text{HalB complexes with F}_2) = -0.053 + 0.093E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.957$$

$$E_{\text{I+BSSE}}(\text{HalB complexes with Cl}_2) = 0.198 + 0.325E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.964$$

$$E_{\text{I+BSSE}}(\text{HalB complexes with Br}_2) = 0.352 + 0.505E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.949$$

$$E_{\text{I+BSSE}}(\text{HalB complexes with FCl}) = 0.789 + 0.806E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.951$$

$$E_{\text{I+BSSE}}(\text{HalB complexes with FBr}) = 0.939 + 1.164E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.927$$

$$E_{\text{I+BSSE}}(\text{HalB complexes with ClBr}) = 0.447 + 0.619E_{\text{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.952$$

This indicates a direct relation between the ability of the electron donor to form charge-transfer complexes and their basicity in the gas phase denoted by the strength of their HB. A related experimental correlation has been described in the literature between the free energy of I_2 complexation in a series of sulfur compounds and their corresponding proton affinities in the gas phase.⁵⁰

An acceptable linear correlation is obtained between the corrected interaction energies at the MP2 level and the experimental intermolecular stretching constants, k , of these

TABLE 2: Calculated Interaction Energy, E_I , BSSE Correction, and Corrected Interaction Energy, E_{I+BSSE} (kcal/mol)

	E_I			BSSE			E_{I+BSSE}		
	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**
FH...FH			-4.75			0.97			-3.78
FH...OH ₂			-9.73			2.19			-7.54
FH...NH ₃			-13.37			2.20			-11.17
FH...CO			-3.58			0.57			-3.01
FH...NCH			-7.27			0.76			-6.51
FH...HCCH			-4.40			1.26			-3.14
FF...FH	-2.36	-0.56	-1.01	2.09	0.30	0.67	-0.27	-0.26	-0.34
FF...OH ₂	-3.13	-2.29	-2.11	1.87	0.75	1.44	-1.26	-1.54	-0.67
FF...NH ₃	-5.02	-8.71	-2.54	1.65	1.00	1.44	-3.37	-7.71	-1.10
FF...CO	-1.24	-0.73	-0.85	0.98	0.28	0.52	-0.26	-0.45	-0.33
FF...NCH	-1.25	-1.01	-1.31	0.71	0.25	0.57	-0.54	-0.76	-0.74
FF...HCCH	-2.11	-1.92	-1.63	1.39	0.44	1.24	-0.72	-1.48	-0.39
ClCl...FH	-4.20	-1.24	-1.56	3.16	0.26	0.73	-1.04	-0.98	-0.83
ClCl...OH ₂	-6.22	-3.52	-3.41	2.20	0.61	1.40	-4.02	-2.91	-2.01
ClCl...NH ₃	-11.19	-8.39	-5.39	1.25	0.78	1.78	-9.94	-7.61	-3.61
ClCl...CO	-2.11	-1.11	-1.48	1.04	0.28	0.63	-1.07	-0.83	-0.85
ClCl...NCH	-2.69	-2.11	-2.68	0.72	0.28	0.81	-1.97	-1.83	-1.87
ClCl...HCCH	-3.02	-1.81	-2.35	0.88	0.31	1.27	-2.14	-1.50	-1.08
BrBr...FH	-5.72	-1.56	-1.87	4.39	0.17	0.63	-1.33	-1.39	-1.24
BrBr...OH ₂	-8.08	-4.21	-4.25	3.64	0.49	1.28	-4.44	-3.72	-2.97
BrBr...NH ₃	-12.86	-9.41	-7.47	3.22	0.63	1.83	-9.64	-8.78	-5.64
BrBr...CO	-3.83	-1.25	-1.78	2.58	0.09	0.49	-1.25	-1.16	-1.29
BrBr...NCH	-4.40	-2.70	-3.59	1.91	0.17	0.79	-2.49	-2.53	-2.80
BrBr...HCCH	-5.07	-2.13	-2.82	2.57	0.14	1.12	-2.50	-1.99	-1.70
FCI...FH	-5.77	-2.73	-2.72	3.34	0.46	0.74	-2.43	-2.27	-1.98
FCI...OH ₂	-8.85	-7.13	-6.06	2.27	0.86	1.63	-6.58	-6.27	-4.43
FCI...NH ₃	-14.68	-15.15	-11.28	1.46	0.95	2.42	-13.22	-14.20	-8.86
FCI...CO	-3.85	-3.21	-2.53	1.42	0.37	0.56	-2.43	-2.84	-1.97
FCI...NCH	-4.88	-5.17	-4.85	0.90	0.35	0.74	-3.98	-4.82	-4.11
FCI...HCCH	-4.74	-4.26	-3.62	1.19	0.41	1.37	-3.55	-3.85	-2.25
FBr...FH	-8.05	-3.58	-3.42	4.82	0.36	0.67	-3.23	-3.22	-2.75
FBr...OH ₂	-11.90	-9.13	-8.02	4.31	0.87	1.67	-7.59	-8.26	-6.35
FBr...NH ₃	-18.57	-18.13	-15.56	3.99	0.87	2.40	-14.58	-17.26	-13.16
FBr...CO	-8.04	-6.01	-3.96	4.20	0.48	0.73	-3.84	-5.53	-3.23
FBr...NCH	-7.89	-7.53	-7.03	2.61	0.45	0.89	-5.28	-7.08	-6.14
FBr...HCCH	-8.22	-5.98	-5.11	3.25	0.36	1.45	-4.97	-5.62	-3.66
ClBr...FH	-6.57	-2.10	-2.26	4.34	0.24	0.70	-2.23	-1.86	-1.56
ClBr...OH ₂	-9.49	-5.43	-5.08	3.60	0.64	1.46	-5.89	-4.79	-3.62
ClBr...NH ₃	-15.47	-11.58	-9.00	3.36	0.84	2.09	-12.11	-10.74	-6.91
ClBr...CO	-4.76	-2.01	-2.33	2.73	0.28	0.72	-2.03	-1.73	-1.61
ClBr...NCH	-5.46	-3.80	-4.37	1.93	0.33	0.97	-3.53	-3.47	-3.40
ClBr...HCCH	-6.18	-3.00	-3.39	2.63	0.32	1.40	-3.55	-2.68	-1.99

TABLE 3: Coefficients of the Free-Wilson Model of the Corrected Interaction Energy, E_{I+BSSE} (MP2/6-311++G**), as a Function of the Monomers, and the Proton Affinity of the Electron Donor Moieties

monomer	Y_i coeff (kcal/mol)	monomer	Y_i coeff (kcal/mol)	exptl ⁴⁹ proton affinity (kcal/mol)
FF	0.9	FH	0.0 ^a	117.0
ClCl	-0.2	OH ₂	-1.9	166.5
BrBr	-1.1	NH ₃	-5.1	204.0
FCI	-2.4	CO	-0.1	141.7
FBr	-4.3	NCH	-1.7	171.0
ClBr	-1.6	HCCH	-0.4	153.3

^a By definition.

complexes, as shown in Figure 3. The following equation for the 19 cases experimentally available was obtained, with a good correlation coefficient and a small standard deviation:

$$E_{I+BSSE} = -(0.270 \pm 0.007)k; \quad r^2 = 0.989; \quad SD = 0.4; \\ N = 19$$

Electronic Properties. One of the most characteristic properties of these complexes is the charge transfer between the interacting monomers, as has been calculated using the AIM methodology (Table 4). The expected electron transfer from

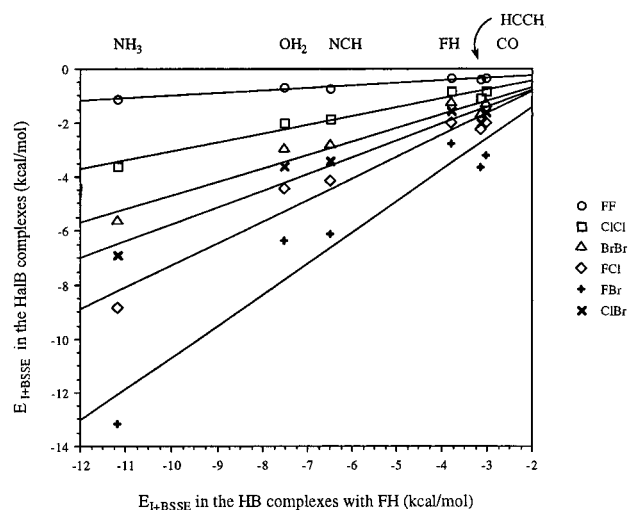


Figure 2. Linear correlation between the interaction energies of each series of HalB complexes and the corresponding HB ones.

the electron donor to the electron acceptor is observed for most of the complexes. The exceptions are those where FH acts as electron donor. In two of these cases (FH...FH and F₂...FH) it acts as electron donor, with very small electronic loss, but it

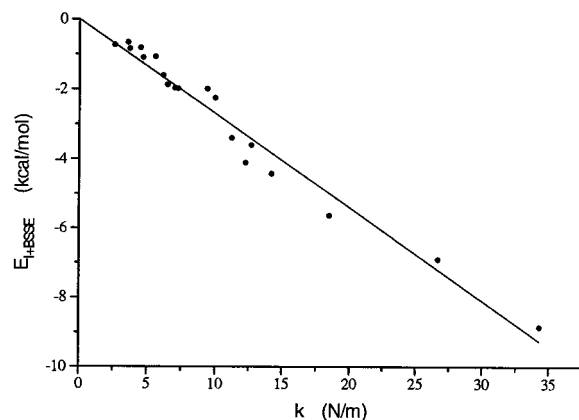


Figure 3. Calculated corrected interaction energy, E_{I+BSSE} , at the MP2/6-311++G** level vs experimental intermolecular stretching force constant, k .

TABLE 4: Charge Transfer (e), within the AIM Methodology, and Dipole Moment (D) of the Calculated Monomers and Complexes at the MP2/6-311++G Level**

system	charge transfer	dipole moment	system	charge transfer	dipole moment
FF		0.00	ClCl...CO	-0.009	0.63
ClCl		0.00	ClCl...NCH	-0.010	3.73
BrBr		0.00	ClCl...HCCH	-0.022	0.45
FCI	1.35	BrBr...FH	0.005	2.31	
FBr	1.83	BrBr...OH ₂	-0.012	3.06	
ClBr	0.52	BrBr...NH ₃	-0.088	4.43	
FH	1.97	BrBr...CO	-0.010	0.85	
OH ₂	2.19	BrBr...NCH	-0.012	4.13	
NH ₃	1.74	BrBr...HCCH	-0.026	0.76	
CO	0.28	FCI...FH	0.000	3.33	
HCN	3.00	FCI...OH ₂	-0.027	4.06	
HCCH	0.00	FCI...NH ₃	-0.157	5.92	
FH...FH	-0.008	3.68	FCI...CO	-0.019	2.20
FH...OH ₂	-0.034	4.49	FCI...NCH	-0.023	5.33
FH...NH ₃	-0.064	4.80	FCI...HCCH	-0.040	2.07
FH...CO	-0.023	2.84	FBr...FH	0.001	3.86
FH...NCH	-0.030	5.86	FBr...OH ₂	-0.025	5.33
FH...HCCH	-0.033	2.53	FBr...NH ₃	-0.163	6.95
FF...FH	-0.003	2.02	FBr...CO	-0.043	3.19
FF...OH ₂	-0.012	2.24	FBr...NCH	-0.039	6.38
FF...NH ₃	-0.038	2.13	FBr...HCCH	-0.061	3.08
FF...CO	-0.011	0.40	ClBr...FH	0.004	2.73
FF...NCH	-0.011	3.21	ClBr...OH ₂	-0.016	3.54
FF...HCCH	-0.025	0.16	ClBr...NH ₃	-0.100	5.02
ClCl...FH	0.003	2.23	ClBr...CO	-0.018	1.41
ClCl...OH ₂	-0.011	2.74	ClBr...NCH	-0.015	4.69
ClCl...NH ₃	-0.069	3.47	ClBr...HCCH	-0.031	1.32

is clearly "harder" than the rest of the electron donors treated here. In the rest of the cases, the acceptor fluorine atom gains small amounts of electronic population, more so when it interacts with the more polarizable and less polar dihalogen. These results are in agreement with the experimental data that indicate that the FH complexes are a borderline case, forming in some cases only HB complexes ($F_2 \cdots HF$, $Br_2 \cdots HF$, and $FBr \cdots HF$), a mixture with HalB complexes ($Cl_2 \cdots FH$ and $Cl_2 \cdots HF$), or mainly a HalB complex ($FCI \cdots FH$).⁵¹

The charge transferred, especially in the complexes with NH_3 , is very large (0.16 e in the complexes with FCl and FBr), indicating the formation of a highly dipolar complex. This effect is clearly confirmed by the large dipole moment of those complexes (Table 4). In fact, several of the complexes of NH_3 with different dihalogen molecules (Cl_2 , Br_2 , $ClBr$, FBr , and $ClBr$) possess a dipole moment that is more than twice the value of the sum of the isolated monomers. This is an indication of a strong polarization of the systems.

TABLE 5: Electron Density (e/au^3), ρ_{bcp} , Laplacian (e/au^5), $\nabla^2\rho_{bcp}$, at the Bond Critical Points and Distance from That Point to the Atoms Involved in the Interaction (Å) at the MP2/6-311++G Level**

syst (X-Y...Z)	ρ_{bcp}	$\nabla^2\rho_{bcp}$	$r_{Y \cdots bcp}$	$r_{bcp \cdots Z}$
FH...FH	0.0206	0.0990	0.657	1.220
FH...OH ₂	0.0366	0.1415	0.560	1.171
FH...NH ₃	0.0501	0.1196	0.519	1.184
FH...CO	0.0177	0.0609	0.710	1.422
FH...NCH	0.0270	0.1012	0.620	1.267
FH...HCCH	0.0158	0.0529	0.747	1.562
FF...FH	0.0073	0.0389	1.295	1.421
FF...OH ₂	0.0221	0.0534	1.221	1.421
FF...NH ₃	0.0164	0.0695	1.165	1.430
FF...CO	0.0062	0.0268	1.351	1.653
FF...NCH	0.0082	0.0381	1.286	1.519
FF...HCCH	0.0081	0.0333	1.314	1.700
ClCl...FH	0.0089	0.0430	1.535	1.383
ClCl...OH ₂	0.0155	0.0626	1.423	1.359
ClCl...NH ₃	0.0273	0.0899	1.306	1.316
ClCl...CO	0.0082	0.0322	1.581	1.599
ClCl...NCH	0.0122	0.0503	1.480	1.440
ClCl...HCCH	0.0087	0.0322	1.587	1.699
BrBr...FH	0.0089	0.0393	1.613	1.400
BrBr...OH ₂	0.0168	0.0617	1.472	1.352
BrBr...NH ₃	0.0318	0.0907	1.329	1.295
BrBr...CO	0.0094	0.0332	1.630	1.578
BrBr...NCH	0.0141	0.0525	1.519	1.420
BrBr...HCCH	0.0100	0.0339	1.634	1.673
FCI...FH	0.0115	0.0541	1.438	1.342
FCI...OH ₂	0.0221	0.0888	1.304	1.285
FCI...NH ₃	0.0508	0.1423	1.138	1.174
FCI...CO	0.0127	0.0488	1.442	1.495
FCI...NCH	0.0184	0.0752	1.346	1.352
FCI...HCCH	0.0124	0.0464	1.466	1.611
FBr...FH	0.0125	0.0549	1.482	1.337
FBr...OH ₂	0.0245	0.1003	1.295	1.277
FBr...NH ₃	0.0526	0.1285	1.170	1.188
FBr...CO	0.0217	0.0722	1.381	1.378
FBr...NCH	0.0252	0.0929	1.329	1.296
FBr...HCCH	0.0172	0.0584	1.458	1.545
ClBr...FH	0.0097	0.0427	1.579	1.384
ClBr...OH ₂	0.0186	0.0684	1.435	1.331
ClBr...NH ₃	0.0350	0.0979	1.296	1.274
ClBr...CO	0.0106	0.0376	1.587	1.549
ClBr...NCH	0.0157	0.0589	1.478	1.396
ClBr...HCCH	0.0110	0.0374	1.599	1.651

The values of the electron density at the bond critical points, ρ_{bcp} , as well as the Laplacian, $\nabla^2\rho$ (Table 5), indicate that these complexes correspond to open shell interactions. The ρ_{bcp} obtained for the complexes with heterodihalogen are similar to the ones corresponding to the HBs formed by FH with the different electron donors. The complexes with homodihalogen show the smallest values of ρ_{bcp} ; however, they are still in the range of weak HBs (for instance 0.0093 e/au^3 for the FH...benzene complex).

Another characteristic that has been compared between the HB and the HalB is the topology of the electron density. Except in cases where the electron donor is HCCH, the bond path connecting the two interacting atoms is almost linear. The position of the bcp between the two interacting atoms moves closer to the electron donor atom as the polarity of the electron acceptor increases. Thus, the position of the bcp is closer to the electron donor atoms in the FH complexes followed by FBr, FCl, and ClBr, and the farthest correspond to the homodihalogen complexes.

In the complexes with HCCH, the topology of the HBs has been described as a catastrophic configuration⁹ and the same is observed here for the HalB (as example, the FBr...HCCH complex is represented in Figure 4). This configuration presents

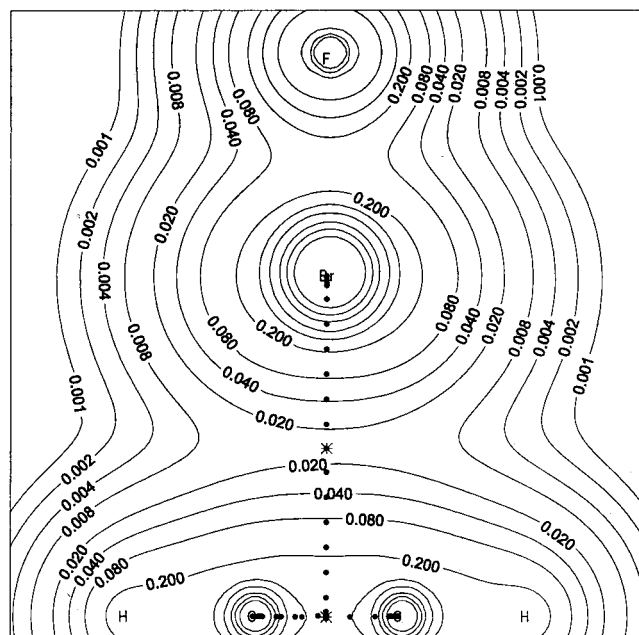


TABLE 7: Dihalogen Bond (X–H Bond in the HB Complexes) Harmonic Stretching Frequencies (cm⁻¹) in the Isolated Monomers and Complexes Calculated at the MP2/6-311++G Level, the Variation Observed, Δ , with Respect to the Isolated Monomers, and the Percent Variation Weighted to the Absolute Value of the Monomer Frequency, % Variation**

monomers	stretching freq	monomers	stretching freq
FH	4197	FCl	733
FF	899	FBr	636
ClCl	546	ClBr	444
BrBr	330		
complexes	stretching freq	Δ	% variation
FH...FH	4104	-93	-2.2
FH...OH ₂	3851	-346	-8.2
FH...NH ₃	3481	-716	-17.1
FH...CO	4068	-129	-3.1
FH...NCH	3958	-239	-5.7
FH...HCCH	4041	-156	-3.7
FF...FH	891	-8	-0.8
FF...OH ₂	874	-25	-2.7
FF...NH ₃	812	-87	-9.6
FF...CO	886	-13	-1.4
FF...NCH	879	-20	-2.2
FF...HCCH	864	-35	-3.9
ClCl...FH	543	-3	-0.6
ClCl...OH ₂	532	-14	-2.5
ClCl...NH ₃	480	-65	-12.0
ClCl...CO	540	-6	-1.0
ClCl...NCH	534	-12	-2.2
ClCl...HCCH	532	-13	-2.5
BrBr...FH	329	-1	-0.3
BrBr...OH ₂	322	-8	-2.3
BrBr...NH ₃	290	-39	-12.0
BrBr...CO	326	-4	-1.2
BrBr...NCH	323	-7	-2.1
BrBr...HCCH	320	-10	-2.9
FCl...FH	727	-6	-0.9
FCl...OH ₂	703	-30	-4.1
FCl...NH ₃	589	-145	-19.7
FCl...CO	715	-19	-2.6
FCl...NCH	705	-28	-3.9
FCl...HCCH	698	-35	-4.8
FBr...FH	632	-4	-0.6
FBr...OH ₂	613	-23	-3.7
FBr...NH ₃	552	-85	-13.3
FBr...CO	615	-21	-3.3
FBr...NCH	613	-23	-3.6
FBr...HCCH	604	-32	-5.0
ClBr...FH	442	-2	-0.5
ClBr...OH ₂	432	-12	-2.7
ClBr...NH ₃	390	-54	-12.1
ClBr...CO	438	-6	-1.4
ClBr...NCH	433	-11	-2.5
ClBr...HCCH	431	-13	-3.0

largest variations are observed when the electron donor is NH₃ > C₂H₂ > OH₂ > NCH > CO > FH. This tendency holds for all the HalB complexes studied. In the case of the HB complexes, the same tendency is observed except for the C₂H₂ case, whose effect is smaller than that of NCH.

The numerical analysis of these variations with respect to the absolute value of the stretching frequency in the monomers (given as a percentage in Table 7) shows striking similarities for each electron donor through the HalB series studied. Thus, the variations observed are in the following ranges: 0.9–0.3 (FH as electron donor), 3.3–1.0 (CO), 3.9–2.1 (NCH), 4.1–2.3 (OH₂), 5.0–2.5 (C₂H₂), and 19.7–9.6% (NH₃). The upper limit corresponds to a complex with a heterodihalogen and the lower one to a complex with a homodihalogen.

The absolute NMR shieldings of the HB and HalB complexes are gathered in Table 8. In contrast to the uniform shift of the

TABLE 8: Absolute NMR Shieldings (ppm) of the Atom in the Electron Acceptor Monomers Involved in the Interaction (in Italics) Calculated Using the GIAO Perturbation Theory at the B3LYP/6-311++G Level**

σ monomers	NMR shielding		σ monomers	NMR shielding	
<i>FH</i>	30.2		<i>FCl</i>	-726.5	
<i>FF</i>	-247.3		<i>FBr</i>	-1908.5	
<i>ClCl</i>	449.5		<i>ClBr</i>	793.0	
<i>BrBr</i>	1502.9				
σ complexes	NMR shielding	$\Delta \sigma$	σ complexes	NMR shielding	$\Delta \sigma$
<i>FH</i> ... <i>FH</i>	28.1	2.2	<i>BrBr</i> ... <i>CO</i>	1546.1	-43.1
<i>FH</i> ... <i>OH</i> ₂	25.4	4.8	<i>BrBr</i> ... <i>NCH</i>	1427.5	75.5
<i>FH</i> ... <i>NH</i> ₃	22.8	7.4	<i>BrBr</i> ... <i>HCCH</i>	1654.3	-151.4
<i>FH</i> ... <i>CO</i>	29.2	1.1	<i>FCl</i> ... <i>FH</i>	-682.0	-44.4
<i>FH</i> ... <i>NCH</i>	27.7	2.6	<i>FCl</i> ... <i>OH</i> ₂	-507.6	-218.9
<i>FH</i> ... <i>HCCH</i>	28.1	2.1	<i>FCl</i> ... <i>NH</i> ₃	-135.3	-591.1
<i>FF</i> ... <i>FH</i>	-253.9	6.6	<i>FCl</i> ... <i>CO</i>	-440.6	-285.9
<i>FF</i> ... <i>OH</i> ₂	-285.6	38.3	<i>FCl</i> ... <i>NCH</i>	-575.8	-150.7
<i>FF</i> ... <i>NH</i> ₃	-193.2	-54.1	<i>FCl</i> ... <i>HCCH</i>	-411.8	-314.7
<i>FF</i> ... <i>CO</i>	-261.1	13.8	<i>FBr</i> ... <i>FH</i>	-1587.9	-320.6
<i>FF</i> ... <i>NCH</i>	-298.8	51.5	<i>FBr</i> ... <i>OH</i> ₂	-909.6	-998.9
<i>FF</i> ... <i>HCCH</i>	-214.2	-33.2	<i>FBr</i> ... <i>NH</i> ₃	124.2	-2032.7
<i>ClCl</i> ... <i>FH</i>	424.3	25.2	<i>FBr</i> ... <i>CO</i>	331.6	-2240.1
<i>ClCl</i> ... <i>OH</i> ₂	428.7	20.8	<i>FBr</i> ... <i>NCH</i>	-787.5	-1121.0
<i>ClCl</i> ... <i>NH</i> ₃	483.5	-34.0	<i>FBr</i> ... <i>HCCH</i>	-454.9	-1453.6
<i>ClCl</i> ... <i>CO</i>	448.0	1.5	<i>ClBr</i> ... <i>FH</i>	767.9	25.1
<i>ClCl</i> ... <i>NCH</i>	399.1	50.4	<i>ClBr</i> ... <i>OH</i> ₂	889.5	-96.5
<i>ClCl</i> ... <i>HCCH</i>	484.5	-35.0	<i>ClBr</i> ... <i>NH</i> ₃	1235.1	-442.1
<i>BrBr</i> ... <i>FH</i>	1440.3	62.6	<i>ClBr</i> ... <i>CO</i>	974.4	-181.5
<i>BrBr</i> ... <i>OH</i> ₂	1474.9	28.0	<i>ClBr</i> ... <i>NCH</i>	834.1	-41.1
<i>BrBr</i> ... <i>NH</i> ₃	1647.4	-144.5	<i>ClBr</i> ... <i>HCCH</i>	1093.6	-300.6

signals to lower fields observed in the hydrogen involved in the HBs, the halogens of the HalB complexes only follow this tendency in some homodihalogenes. The reverse is observed for all the heterodihalogen complexes, except for ClBr...FH in which an important reverse charge transfer is observed, as mentioned before. In addition, while in the HBs the observed effect follows the trend of the interaction energy, where stronger complexes provide larger changes in shielding, in the HalB there is not such relationship; even though, in general, the largest negative effect corresponds to the complexes with NH₃ and the smallest to those with FH.

Conclusions

The geometric, electronic (including the AIM analysis), and spectroscopic properties of a series of charge-transfer complexes formed between dihalogen compounds (F₂, Cl₂, Br₂, FBr, FCl, and ClBr) and electron donor groups (FH, OH₂, NH₃, CO, NCH, and C₂H₂), as well as the HB complexes of FH with the same electron donors, have been calculated. The comparison of these two sets of charge-transfer complexes (HB and HalB complexes) shows some similarities and differences.

The similarities found between HalBs and HBs include to geometrical variation of the monomers in the formation of the complexes, the trend in interaction energy with respect to the electron donor molecule, the electronic properties of the bcp (ρ_{bcp} and $\nabla^2\rho_{\text{bcp}}$), the topology of the electron density, and the changes in the IR signal corresponding to the bond stretching of the dihalogen bond in the HalB complexes and the X–H bond in the HB ones.

The differences observed are the lack of regularities in the variation of the atomic properties calculated for the interacting halogen within the AIM methodology (charge, volume, energy, dipolar polarization) in contrast to the ones observed for the HB complexes. In addition, the changes in the NMR shieldings

of the interacting atom in the HalB are not dependent on the strength of the complexes.

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